1966

The Activity and Other Thermodynamic Properties of Hydrochloric Acid in Monoglyme - Water Mixtures.

David Alfred Johnson
Louisiana State University and Agricultural & Mechanical College

THE ACTIVITY AND OTHER THERMODYNAMIC PROPERTIES OF HYDROCHLORIC ACID IN MONOGLYME-WATER MIXTURES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
David Alfred Johnson
A. B. Greenville College, 1960
August, 1966

ACKNOWLEDGMENT

The author wishes to acknowledge the faithful and loving support of his wife, Jann, during his graduate training. This program could never have been accomplished without her encouragement and help.

The author wishes to thank Dr. B. Sen for directing this work and for his patient counsel and encouragement. He further wishes to thank Dr. R. V. Nauman for his contribution and to other members of the graduate chemistry faculty who made a contribution to the author's training.

Grateful acknowledgment is made to the National Science Foundation for partial financial assistance through two summers of support in the College Teachers' Research Participation Program and an Academic Year Extension Grant. The author further acknowledges financial assistance from the "Dr. Charles E. Coates Memorial Fund of the L. S. U. Foundation donated by Charles H. Coates". Thanks is expressed also to Spring Arbor College, Spring Arbor, Michigan for a faculty scholarship during the academic year 1965 - 1966.

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ABSTRACT

An interest in the problem of the thermodynamics of mixed solvent systems has resulted in the study of the galvanic cell, $H_2|HCl(m)|AgCl\text{-}Ag$, in monoglyme-water mixtures at four temperatures and in acetonitrile-water mixtures at two temperatures.

Ten solutions ranging in hydrochloric acid concentration from 0.1 to 0.001 molal were studied for each solvent system and at each temperature. The E^o values were evaluated for each system by extrapolation of the curve formed by plotting the quantity $E_{obs} + \frac{2RT}{F} \ln m$ versus $m^{1/2}$. The extrapolation was carried out with the use of a polynomial curve fitting program which utilized the least squares technique. By means of the LaMer-Gronwall extension of the Debye and Hückel theory for symmetrical electrolytes, it was shown that an equation analogous to the type used in the polynomial curve fitting program can be obtained.

Results in the acetonitrile-water mixtures were not satisfactory as a steady state at the hydrogen electrode was not attained. The cause of this was thought to be due to the hydrolysis of the acetonitrile by hydrogen ion.

The errors in the E^o values for the monoglyme-water mixtures were estimated to be ±0.2 millivolts for 8.68 and 17.81 percent monoglyme mixtures, ±0.4 millivolts, ±1.0 millivolts and ± several millivolts for 46.52, 67.03 and 88.80 percent monoglyme mixtures, respectively. The mean activity coefficients of hydrochloric acid were calculated and within the limits of experimental error followed

the general trends of other mixed solvent systems. The primary and secondary medium effects were also evaluated. The relative partial molal heat content and heat capacity were evaluated for two systems and followed the trends occurring in other mixed solvents.

CHAPTER I

INTRODUCTION

In studying chemical equilibria, frequently it is necessary to use a mixed solvent system consisting of water and a miscible organic solvent to avoid insolubility, hydrolysis, or other complicating features of the reactants and/or products. For example, Sen and Schuman (32) while studying chelate formation potentiometrically were forced to use a mixed solvent system consisting of acetone and water in order to dissolve metal phenyl-2-pyridyl-ketoximates.

The use of mixed solvents in such studies however creates a fundamental problem when thermodynamic properties are to be calculated. The problem is the result of the choice of the infinitely dilute aqueous state as the basis for the standard reference state in solutions. Normally the thermodynamic properties measured in a given mixed solvent system have the reference state defined by the infinitely dilute state in the mixed solvent system. Practically speaking it is important to know the relative thermodynamic properties in a given mixed solvent, but it would be of greater value if there were a means of converting the values in the mixed solvent system to values referred to the aqueous state.

The research described in this text is part of an overall program to determine the means to make such conversions. Although several mixed solvent systems have been studied previously it was felt that information on systems that contain some of the newer organic solvents in common use today would be advantageous and such studies would be used as a starting point for embarking on the overall goal of the research program.

Several mixed solvent systems have been used in the study of the following general cell

$$H_2(1\ atm.) \mid HCl\ (m),\ Organic\ (X),\ Water\ (Y) \mid AgCl\text{-}Ag \qquad \ldots\ldots 1$$

in which m represents the molality of the hydrochloric acid; X the weight percent of the organic solvent; and Y the weight percent of water.

The most comprehensive series of measurements of the electromotive forces of such cells has been made on dioxane-water mixtures by Harned and his co-workers (12-25). References 12-19 and 21-25 contain the description of the work while reference 20 presents a general summary of all the work.

The cells were studied with 20, 45, 70 and 82 percent dioxane-water mixtures as the mixed solvent systems, at hydrochloric acid concentrations ranging from 0.001 molal to as high as 3 molal in some systems, and at 5°C intervals ranging from 0°C to 50°C. The solvents have dielectric constants of approximately 60, 40, 20 and 10. The electromotive force measurements were reproducible to within ±0.1 mv. with the exception of those of the solutions more concentrated in dioxane. Results consistent to within smaller limits (±0.02 mv.) were obtained in solutions in which the percentage of dioxane was small. The extrapolations necessary to obtain standard electrode potentials were carried out by several methods. Two methods were used for the extrapolations in the 20, 45, and 70 percent mixtures while a third method was necessary to make the extrapolations in the 82 percent mixtures. The first method involved the use of the Debye and Hückel limiting equation without the term for the mean distance of approach (19)

and the second employed the Gronwall-LaMer extension of the Debye and Hückel theory (12, 17). In the 20 percent solvent system both of these methods gave practically the same results (within 0.2mv.) for the standard potentials. All extrapolations were made graphically. As the dielectric constant of the solvent decreased, which corresponded to the increased dioxane percentage, the differences between the results of the two extrapolation methods became greater, being as much as 0.7 mv. in 45 percent dioxane and as much as 2-3 mv in 70 percent dioxane (14). Neither of these methods were suitable for extrapolation purposes in the 82 percent dioxane mixtures. A new method was employed which utilized ionization data derived from conductance measurements at low acid concentrations (25). This new method was necessary for extrapolation because as the dielectric constant of the medium decreases the hydrochloric acid no longer behaves as a strong electrolyte which completely dissociates in solution, but behaves as a weak electrolyte. The authors were unable to estimate the accuracy of this last extrapolation method.

The electromotive force data was tabulated using an equation of the form

$$E = E_{25} + a(t-25) + b(t-25)^2 \qquad \ldots.2$$

in which E is the cell electromotive force at the centigrade temperature, t; E_{25} is the cell electromotive force at 25°C; and a and b are constants. The values of a and b were determined by the method of least squares.

The mean activity coefficients were computed at each temperature and at rounded concentrations of acid for each solvent system. The values decreased with increasing temperature at all concentrations of

acid and for all solvent systems. An extensive analysis of the mean activity coefficient behavior is given in reference 20 and in the text by Harned and Owens (3). It is particularly interesting to examine a plot of the logarithm of the activity coefficient versus the root molality. This plot provides information concerning ion association in the various dioxane mixtures. The most striking characteristic of the results is the general agreement of the observed values with those predicted by Debye and Hückel equation in solutions of low acid concentration. If no ion association takes place, the observed values (in dilute solutions) lie above the limiting slope of the curve which corresponds to the Debye and Hückel law. In the 20 and 45 percent dioxane media all values are above the limiting slope; at 70 percent the activity coefficients coincide with the limiting values. In the 82 percent mixtures the activity coefficients are below the limiting slope indicating ion association.

The values of the relative partial molal heat content of hydrochloric acid, $\bar{L}_2$, were calculated from the electromotive force data. Since the values of the mean activity coefficients decreased with increasing temperature, the values of $\bar{L}_2$ were positive in each case. The calculations were made in the following way. The electromotive force measurements were first smoothed graphically against concentration, and the values were obtained at convenient rounded concentrations. Then the constants of some suitable functions such as equations (3) and (4) were obtained at each concentration by the method of least squares.

$$E = a + bT + cT^2 \qquad \ldots.3$$

$$E^o = a_o + b_oT + c_oT^2 \qquad \ldots.4$$

A plot of experimental $\bar{L}_2$ values versus root molality indicated an increasing tendency for the experimental curves to be higher than the limiting values in dilute solutions as the dioxane content of the mixed solvent increased. All curves had similar characteristics, a rapid rise in dilute solutions followed by a leveling off as the acid concentration increased. The accuracy of the $\bar{L}_2$ values was estimated to be ±30 cal. which is not as good as calorimetric data. The reason for such large errors can be understood when it is realized that an error of 0.001 mv./deg. in the temperature coefficient of the electromotive force gives an error of ±7 cal. in the value of $\bar{L}_2$.

Closely connected with the relative partial molal heat content is the relative partial molal heat capacity, $\bar{J}_2$. In conjunction with $\bar{L}_2$ the values of $\bar{J}_2$ were also calculated. High accuracy cannot be expected since the determination of $\bar{J}_2$ involves the second differential coefficient of the original electromotive force data. Harned estimated that the error was greatest in the 82 percent dioxane mixtures and of the order of 10 $\frac{\text{cal.}}{\text{deg. mole}}$.

Harned and Thomas (22,23) have measured the electromotive forces of cells in which methanol-water mixtures were the solvents. The cells were studied at temperatures ranging from 0° to 40°C. The mixed solvents contained 10 and 20 percent by weight of methanol. The standard electrode potentials were evaluated by employing the Debye and Hückel limiting law for the extrapolation. The mean activity coefficients of hydrochloric acid were calculated and compared with the values obtained from an empirical equation of the type used for calculation of activity coefficients in pure water. The relative partial molal quantities were also calculated.

Cells containing ethanol-water mixtures of 10, 20, 30, 40 and 50 weight percent ethanol have been studied at 25°C (13,15). The standard electrode potentials were obtained, and the mean activity coefficients were evaluated.

Isopropyl alcohol-water mixtures have also been used as mixed solvents in galvanic cells (13, 15, 30). The standard electrode potentials and mean activity coefficients were evaluated at 25°C. It is interesting to note that Moore and Felsing (30) were not able to obtain reversible or reproducible behavior with the hydrogen electrode in n-propyl alcohol-water and acetone-water mixtures. The aim of the work of Moore and Felsing was to study the effect of the length of the aliphatic chain of the alcohol upon the standard electrode potential of the cell.

Galvanic cells having glycerol-water mixtures as the mixed solvent with glycerol compositions of one and five mole percent have been studied at 25°C (29). The mean activity coefficients of hydrochloric acid were calculated and compared with the theoretical values obtained from Hückel's equation which is given in reference 29. A more extensive study was made on cells with 50 percent glycerol mixtures at temperatures ranging from 0° to 90°C (21). No attempt was made to calculate activity coefficients or the relative partial molal quantities from the electromotive force data.

The cell containing ethylene glycol-water mixtures as solvent has been studied at 25°C (9, 27). The compositions of the mixed solvents were 5, 10, 15, 20, 30, 40 and 60 percent by weight of ethylene glycol. Extrapolations were made using the Debye and Hückel

limiting law with the term for mean distance of approach. The mean activity coefficients of hydrochloric acid were calculated. The logarithm of the mean activity coefficient was plotted against the logarithm of the molality, and the activity coefficients at rounded concentrations were read off the graph. It is particularly interesting to notice that the activity coefficients (Appendix, Table A-4) at the low concentration range (<0.012m) are smaller for 10 percent ethylene glycol than for either 20 or 40 percent ethylene glycol. The authors could give no explanation for this anomaly but the last communique (9) showed this anomaly lacking in the 5, 15 and 30 percent ethylene glycol solutions.

Cells containing d-glucose-water mixtures of 5, 10, 20 and 30 percent by weight of d-glucose have been studied at 25°C (34). From the electromotive force data the standard potentials and the ion size parameters of hydrochloric acid were obtained and the mean activity coefficients were calculated and were tabulated.

CHAPTER II

THEORETICAL ASPECTS

A general chemical equation at constant temperature and pressure can be expressed by equation (5).

$$aA + bB \rightleftarrows cC + dD \qquad \ldots.5$$

The total Gibbs free energy change for the reaction in terms of the activities of the reactants and products is given by equation (6).

$$\Delta G = \Delta G^{o} + RT \ln \frac{\pi' a}{\pi a} \qquad \ldots.6$$

where ΔG represents the total free energy change; ΔG^{o}, the total free energy change;when the activities of all the reactants and products are unity; $\pi' a$, the activity product,including the proper exponents,of the products; and, πa, the activity product,including the proper exponents, of the reactants.

In dealing with electrolytes it is convenient to express the activity of an electrolyte in terms of the activities of the ions into which the electrolyte dissociates in solution. If the electrolyte, $C_{\nu^+} A_{\nu^-}$, dissociates into ν^+ cations and ν^- anions according to

$$C_{\nu^+} A_{\nu^-} \rightarrow \nu^+ C + \nu^- A \qquad \ldots.7$$

then the activity of the electrolyte can be expressed as

$$a = a_+^{\nu^+} a_-^{\nu^-} = a_{\pm}^{\nu} \qquad \ldots.8$$

where a_+ and a_- represent the activities of the cation and anion, respectively; $a_{\pm}$ is defined as the mean activity; and ν is equal to the sum of ν^+ and ν^-. The mean molality, $m_{\pm}$, can be defined in a manner similar to the mean activity. In very dilute solutions the value of the

mean activity approaches the value of the mean molality, however, in more concentrated solutions there is a departure from ideality and the mean activity no longer approaches the value of the mean molality. It is convenient to express this departure from ideality in terms of the activity coefficient, a factor defined by equations (9) and (10).

$$\gamma = \frac{a}{m} \qquad \ldots.9$$

$$\gamma_{\pm} = \frac{a_{\pm}}{m_{\pm}} \qquad \ldots.10$$

Equation (9) refers to nonelectrolytes while equation (10) is valid for electrolytes.

It can be shown that the free energy change for a given process at constant temperature, pressure, and composition is related to the reversible electrical work. Consider a cell consisting of two electrodes connected by a solution of an electrolyte. Let $(\psi' - \psi'')$ be the difference in electrical potential between two pieces of the same metal attached to the two electrodes. Thus, if the cell is charged reversibly at constant temperature and pressure, the electrical work done upon the system will be $(\psi' - \psi'')$ de, in which de is the charge transferred which corresponds to a change in free energy, dG. The quantity $(\psi' - \psi'')$ de then is equal to the total increase in free energy.

$$(dG)_{T,P,N} = (\psi' - \psi'')\ de \qquad \ldots.11$$

The mechanism fulfilling the conditions required by equation (11) is a galvanic cell, consisting of two reversible electrodes connected by a solution of the appropriate electrolyte. Equation (11) is valid for reversible changes only. The criteria for reversibility are:

1) No changes take place in the cell without the passage of current.

2) Every change occuring during the infinitesmal passage of current may be reversed by changing the direction of the current.

3) The net result of all chemical changes must be known.

If a cell with an electromotive force of $\pm E$ is exactly balanced against an external electromotive force, then $\pm E$ is the electromotive force of the cell when the entire system is at equilibrium. If the cell is imagined to discharge against this external electromotive force until a quantity of electricity, de, has passed through, the cell process will have taken place reversibly, performing the reversible electrical work, $\pm Ede$. The difference in potential, $(\psi' - \psi'')$, is equal to $+E$ or $-E$ depending on the convention adopted concerning the sign of the electromotive force. In chemical reactions the changes involved are usually expressed on a molar basis, consequently the passage of a faraday, F, or a multiple of a faraday, NF, of charge is involved. Since the free energy change is proportional to de, NF can be substituted for de in equation (11) and $\pm E$ for $(\psi' - \psi'')$ to give equation (12).

$$(\Delta G)_{T,P,N} = -NFE \qquad \ldots.12$$

In writing equation (12) the convention of Lewis and Randall is adopted, in that a positive electromotive force corresponds to a decrease in the free energy.

Substitution of equation (12) into equation (6) and subsequent rearrangement gives the following equation

$$E = E^{o} - \frac{RT}{NF} \ln \frac{\pi' a}{\pi a} \qquad \ldots.13$$

in which $E^{o} = -\frac{\Delta G^{o}}{NF}$ and is called the standard electromotive force of the galvanic cell. It is easily seen that E equals E^{o} when the activities of all constituents are equal to unity. The composition of a solid component of the cell is ordinarily independent of the concentration of the electrolyte solution, and it is customary to consider solids to be in their standard states at all temperatures when pressures are of the order of one atmosphere. The net result is that under normal conditions the activities of solids are unity. Since the partial pressure of a gas in a gaseous mixture is proportional to the concentration, and furthermore since the perfect gas law may be applied for practical purposes over small pressure changes in the neighborhood of one atmosphere, the activity of a gaseous component is written equal to the partial pressure. Thus a gas is in its standard state at any temperature when its partial pressure is one atmosphere. The standard state for the components of liquid solutions is usually selected so that the molality is equal to the activity or the activity coefficient is unity for each solute at infinite dilution. In the case of electrolytes the standard state is selected so that the mean activity is equal to the mean molality or the mean activity coefficient is unity at infinite dilution. Because of this choice of standard state, the standard state for electrolytes is a hypothetical one.

In order to develop the necessary theory for the study of galvanic cells consider the cell designated by equation (14). This cell differs from the cell in equation (1) by the absence of an organic solvent or in that X, the weight percent of organic solvent is equal to zero

and in that the pressure of hydrogen gas is not necessarily one atmosphere.

$$H_2(p \text{ atm.}) \mid HCl(m) \mid AgCl\text{-}Ag \qquad \ldots.14$$

In equation (14) p represents the partial pressure of the hydrogen gas and m represents the molality of the hydrochloric acid in moles of acid per kilogram of water. The cell reaction is given in equation (15).

$$\frac{1}{2} H_2(g) + AgCl(s) = Ag(s) + HCl(m) \qquad \ldots.15$$

Since only one mole of electrons is involved in the overall reaction, the electromotive force of the cell is given by equation (16).

$$E = E^o - \frac{RT}{F} \ln \frac{(a_{Ag})(a_{HCl})}{(a_{AgCl})(a_{H_2})^{\frac{1}{2}}} \qquad \ldots.16$$

Making use of the conventions regarding standard states of solids which has just been discussed, equation (16) becomes equation (17).

$$E = E^o - \frac{RT}{F} \ln \frac{a_{HCl}}{(p_{H_2})^{\frac{1}{2}}} \qquad \ldots.17$$

To avoid the necessity of recording the partial pressure of hydrogen gas involved in the cell reaction, it is convenient to convert electromotive forces measured at a partial pressure, p, to values corresponding to a partial pressure of one atmosphere. This is done in the following manner. The electromotive force of the given cell with hydrogen at a partial pressure, p, is given by equation (18).

$$E_{(p)} = E^o - \frac{RT}{F} \ln a_{HCl} + \frac{RT}{2F} \ln p_{H_2} \qquad \ldots.18$$

The electromotive force of the same cell with hydrogen at a partial pressure of one atmosphere is given by equation (19).

$$E_{(1)} = E^{o} - \frac{RT}{F} \ln a_{HCl} + \frac{RT}{2F} \ln 1 \text{ atm.} \quad \ldots.19$$

The difference in the electromotive forces due to the difference in the partial pressure of hydrogen is the difference between equations (19) and (18).

$$E_{(1)} - E_{(p)} = \Delta E = \frac{RT}{2F} \ln \frac{760}{P-p_s} \quad \ldots.20$$

The quantity ΔE in equation (20) represents the increment which must be added to the electromotive force measured at a hydrogen partial pressure of p to obtain the value corresponding to a hydrogen partial pressure of one atmosphere; P represents the barometer pressure; and p_s the partial pressure of the solvent. In most work the quantity $E_{(1)}$ in equations (19) and (20) is called E observed and this practice will be adherred to in this work.

Assuming that the electromotive force of the cell has been converted to the value corresponding to a hydrogen partial pressure of one atmosphere, then the activity of hydrochloric acid can be treated. The activity of hydrochloric acid can be expressed in terms of the mean activity coefficients and mean molalities of hydrogen ion and chloride ion. From equations (8) and (10) and the fact that hydrochloric acid is a 1 - 1 electrolyte, equation (21) is obtained.

$$a_{HCl} = (a_{H^+})(a_{Cl^-}) = (a_{\pm})^2 = \gamma_{\pm}^2 m_{\pm}^2 = \gamma_{\pm}^2 m^2 \quad \ldots.21$$

In the cell indicated by equation (14), the mean concentration is the same as the concentration of the hydrochloric acid in the cell, hence m is used for $m_{\pm}$ in equation (21). Combining equation (21) with the equation for the corrected electromotive force, equation (22) is obtained.

$$E_{(obs)} = E^{o} - \frac{2RT}{F} \ln \gamma_{\pm} m \quad \ldots.22$$

Rearrangement of equation (22) gives the following equation.

$$- E_{(obs)} + \frac{2RT}{F} \ln m = E^{o} - \frac{2RT}{F} \ln \gamma_{\pm} \quad \ldots.23$$

Equation (23) can be used to obtain E^{o}. As the molality approaches zero, the mean activity coefficient approaches unity, causing the logarithmic term on the right hand side of equation (23) to approach zero. Thus the entire left hand side of equation (23) approaches E^{o} as the molality approaches zero. If the left hand side of equation (23) is plotted versus some function of molality, an extrapolation to zero concentration can be made and the value of E^{o} obtained. In practice it is convenient to use the square root of the molality as this tends to compress the curve and make extrapolation easier.

This type of extrapolation is somewhat difficult to carry out with great accuracy because a nonlinear extrapolation is necessary. This can be remedied by using the expression derived by Debye and Hückel for the logarithm of the mean activity coefficient of an electrolyte,

$$\ln \gamma_{\pm} = -S_{(f)} \Gamma + B'm \quad \ldots.24$$

where $S_{(f)}$ is a constant containing several factors including the dielectric constant of the media and temperature, Γ represents the so-called ional concentration and is defined by Harned and Owens (3) and B' is a constant. Combining equations (24) and (23) gives a new equation for extrapolation purposes.

$$E_{(obs)} + \frac{2RT}{F} \ln m - \frac{2RT}{F} S_{(f)} \Gamma = E^{o} - \frac{2RT}{F} B'm \quad \ldots.25$$

A plot of the left hand side of equation (25) versus root molality gives a more nearly linear plot resulting in a more accurate extrapolation. An additional improvement to equation (25) can be made by considering the extension of the Debye and Hückel theory as worked out by Gronwall and LaMer (11,28). Unfortunately, it is necessary to know the value of the dielectric constant of the solvent to make use of equation (25) or any other similar expression.

It is necessary now to study the energy changes which accompany the transfer of a strong acid from one solvent medium to another. Consider the galvanic cell represented by equation (1).

$$H_2(1\ \text{atm.}) \mid HCl(m),\ \text{Organic (X)},\ \text{Water (Y)} \mid AgCl\text{-}Ag \qquad \ldots.1$$

As a first consideration let X = 0, or in other words, consider the cell with water as the solvent. This cell has been extensively studied by several workers (3). The electromotive force of such a cell is given by equation (22). Since cells containing mixed solvent systems will be considered it is convenient to introduce a set of notations to be able to keep track of the various cells considered (2,6). For the cell containing only water equation (22) can be expressed in the following manner:

$$E_w = E_w^o - \frac{2RT}{F} \ln {}_w\gamma_{\pm}\, m \qquad \ldots.26$$

The superscripts indicate the medium in which the measurements are made, in this case w represents water. The subscripts indicate that the mean activity coefficient is measured relative to unity at infinite dilution in that medium and again the w indicates the activity coefficient is measured relative to unity at infinite dilution in water. To avoid

additional subscripts it will be assumed from here on that E corresponds to the $E_{(obs)}$ of equation (22).

Now consider the case when X does not equal zero, or when there is a mixture of an organic solvent and water. There are numerous ways in which the standard state can be defined in mixed solvent systems (6).

1) The infinitely dilute state in the mixed solvent system can be used to define the standard state. This means the activity coefficient is measured relative to unity at infinite dilution in the mixed solvent. This can be expressed symbolically in the following manner:

$$\underset{s}{}^{s}\gamma_{\pm} \rightarrow 1 \text{ as } m \rightarrow 0.$$

This will give one value for the standard electrode potential which can be expressed symbolically as $^{s}E^{o}$.

2) The standard state can be defined by the infinitely dilute state in pure water. In this case the standard electrode potential is expressed as $^{w}E^{o}$.

3) The infinitely dilute state in the pure organic solvent can be used to define the standard state in the mixed solvent system.

If the first method of defining the standard state in mixed solvents is used the electromotive force of the cell containing the mixed solvent can be expressed by the following equation:

$$^{s}E = {}^{s}E^{o} - \frac{2RT}{F} \ln \underset{s}{}^{s}\gamma_{\pm}\, m \qquad \ldots.27$$

Equation (27) can be rearranged to give an equation similar to equation (23). The limit of such an equation as the molality approaches zero is equation (28).

$$ {}^{s}E^{o} = \lim_{m \to 0} \left[{}^{s}E + \frac{2RT}{F} \ln m \right] \qquad \ldots.28 $$

On the other hand it might be desired to choose to define the standard state in the mixed solvent in another way. If the mixed solvent is thought to be nothing more than the aqueous cell to which a certain amount of organic solvent has been added, then since the aqueous cell has been studied so thoroughly, ${}^{w}E^{o}$ may be retained and the electromotive force of the cell will be given by

$$ {}^{s}E = {}^{w}E^{o} - \frac{2RT}{F} \ln {}_{w}^{s}\gamma_{\pm} \, m \qquad \ldots.29 $$

where the standard state is defined by the infinitely dilute state in pure water. In this case the mean activity coefficient is calculated on the basis that it is unity at infinite dilution in pure water; whereas in the first case the mean activity coefficient is calculated on the basis that it is unity at infinite dilution in the mixed solvent. At infinite dilution in the mixed solvent equation (29) becomes

$$ {}^{w}E^{o} = \lim_{m \to 0} \left[{}^{s}E + \frac{2RT}{F} \ln m + \frac{2RT}{F} \ln {}_{w}^{s}\gamma_{\pm} \right] \qquad \ldots.30 $$

where the logarithm of the mean activity coefficient no longer approaches zero as the molality approaches zero.

The standard state in the mixed solvent can be defined in still another way corresponding to the third method listed previously. However, little work has been done in the area of cells containing only pure organic solvents so it is better to use the first two methods to define the standard state in the mixed solvent. If, however, such studies have been carried out there is no reason not to make use of third way of defining the standard state and obtain an expression for

the electromotive force of the cell containing the mixed solvent as has been done in equation (29).

If equation (28) is subtracted from equation (30) and recalling that ${}^{s}E$ is the same in each equation the following equation is obtained

$$({}^{w}E^{o} - {}^{s}E^{o}) = \lim_{m \to 0} \left[\frac{2RT}{F} \ln {}^{s}_{w}\gamma_{\pm}\right] = \frac{2RT}{F} \ln {}^{s}_{w}\gamma_{o\pm} \qquad \ldots.31$$

where ${}^{s}_{w}\gamma_{\pm o}$ represents the mean activity coefficient of hydrochloric acid at infinite dilution in the mixed solvent referred to unit value in infinite dilution in pure water. Both ${}^{w}E^{o}$ and ${}^{s}E^{o}$ can be obtained from experimental measurements so ${}^{s}_{w}\gamma_{\pm o}$ can be evaluated.

At infinite dilution in any medium the interionic effects are absent. Equation (31) then is a measure of the effect of transferring a pair of ions from one solvent to another under conditions where only solvent-ion interactions are operative. This effect has been defined by Owen (31) as the primary medium effect. Since the primary medium effect is measured at infinite dilution it is independent of the hydrochloric acid concentration..

There is another medium effect which is defined and designated by Owen as the secondary medium effect. To illustrate the secondary medium effect consider the following cell

$$\text{Ag-AgCl}\,|\,\text{HCl(m), Water}\,|\,\text{H}_2\text{(1 atm.)}\,|\,\text{HCl(m), Organic (X), Water(Y)}\,|\,\text{AgCl-Ag} \qquad \ldots.32$$

where m, the molality of the hydrochloric acid, is the same in both solvents. The cell reaction involves the transfer of hydrochloric acid from the aqueous system to the mixed solvent system. The electromotive force of the whole cell can be expressed as

$$E_{cell} = {}^{s}E - {}^{w}E = {}^{s}E^{o} - {}^{w}E^{o} - \frac{2RT}{F} \left[\ln {}^{s}_{s}\gamma_{\pm} - \ln {}^{w}_{w}\gamma_{\pm}\right] \qquad \ldots.33$$

by making use of equations (27) and (26). By making the acid concentration the same in each solvent any energy change due to concentration changes is eliminated; that is to say the energy change is zero except for changes dependent on departures from the laws of ideal solutions (6).

Equation (33) represents a complicated operation. It represents the transfer of hydrochloric acid from a finite concentration in water to infinite dilution in water, its transfer from the infinitely dilute state in water to the infinitely dilute state in the mixed solvent and finally a transfer from infinite dilution in the mixed solvent to a finite concentration in the mixed solvent.

The electromotive force of this double cell could be equally well expressed using equations (29) and (26).

$$E_{cell} = {}^{s}E - {}^{w}E = - \frac{2RT}{F} \left[\ln {}^{s}_{w}\gamma_{\pm} - \ln {}^{w}_{w}\gamma_{\pm} \right] \qquad \ldots.34$$

Combining equations (34) and (33) and making use of equation (31) the following relationship is obtained:

$$E_{cell} = {}^{s}E - {}^{w}E = - \frac{2RT}{F} \ln {}^{s}_{w}\gamma_{o\pm} - \frac{2RT}{F} \ln \frac{{}^{s}_{s}\gamma_{\pm}}{{}^{w}_{s}\gamma_{\pm}} = - \frac{2RT}{F} \ln \frac{{}^{s}_{s}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}} \qquad \ldots.35$$

Further simplification and rearrangement gives equation (36).

$$\ln \frac{{}^{s}_{s}\gamma_{\pm}}{{}^{w}_{s}\gamma_{\pm}} = \ln {}^{s}_{w}\gamma_{o\pm} + \ln \frac{{}^{s}_{s}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}} \qquad \ldots.36$$

Owen (31) defines the term on the left hand side of equation (36) as the total medium effect. As previously stated Owen defines $\ln {}^{s}_{w}\gamma_{\pm o}$ as theprimary medium effect. The last term on the right hand side of equation (36) he defines as the secondary medium effect. Equation (36) therefore gives the definitional relationship between the total, primary and secondary medium effects.

The total medium effect is total in the sense that it is a measure of the total change in chemical potential accompanying the movement of hydrochloric acid at finite but equal concentration in two solvents. As indicated by equation (36) this total medium effect is composed of the primary and secondary medium effects. The primary medium effect is determined by the difference in the ion-solvent interactions at infinite dilution in each solvent. The primary medium effect can be expressed as

$$\ln \frac{{}^{s}_{w}\gamma_{o\pm}}{{}^{w}_{w}\gamma_{o\pm}},$$

but since ${}^{w}_{w}\gamma_{\pm o}$ is equal to unity the expression reduces to $\ln {}^{s}_{s}\gamma_{\pm o}$. The significance of the secondary medium effect follows: ${}^{s}_{s}\gamma_{\pm o}$ measures the difference in the 'nonideal' part of the chemical potential of hydrochloric acid at finite concentration and at infinite dilution in the mixed or nonaqueous solvent. It will be given by some form of the Debye and Hückel equation, and one factor which will be important is the dielectric constant of the solvent. ${}^{w}_{w}\gamma_{\pm}$ on the other hand measures the 'nonideal' part for the same concentration change in pure water.

These considerations can be summarized as follows: The total medium effect on the transfer of an electrolyte from a finite concentration in one solvent to a similar concentration in another solvent is a composite one. The secondary medium effect results mainly from a difference in ion-ion interactions in the two solvents and is determined to a large degree by the dielectric constant of each medium. The primary medium effect is independent of concentration and results from a difference of the ion-solvent interactions; it should also be

largely dependent on the dielectric constant of the medium (6).

Consider now the effect of an organic solvent on the ionization constant of a weak electrolyte. The thermodynamic ionization constant of a weak acid, HR, in water is given by

$$ {}^{w}K_A = \frac{{}^{w}\gamma_H \; {}^{w}\gamma_R}{{}^{w}\gamma_{HR}} \cdot \frac{m_H \, m_R}{m_{HR}} \qquad \ldots.37 $$

in which the superscript w indicates the measurement is made in pure water. In a different solvent equation (37) can be expressed as

$$ {}^{s}K_A = \frac{{}^{s}\gamma_H \; {}^{s}\gamma_R}{{}^{s}\gamma_{HR}} \cdot \frac{m_H \, m_R}{m_{HR}} \qquad \ldots.38 $$

in which the superscript s indicates the measurement was made in a medium other than pure water.

If the quantity $\ln {}^{w}_{w}\gamma_{\pm}$ is subtracted from equation (36) the following expression is obtained.

$$ \ln {}^{s}_{w}\gamma_{\pm} = \ln {}^{s}_{w}\gamma_{\pm o} + \ln {}^{s}_{s}\gamma_{\pm} \quad \text{or} \quad {}^{s}_{w}\gamma_{\pm} = {}^{s}_{w}\gamma_{\pm o} \; {}^{s}_{s}\gamma_{\pm} \qquad \ldots.39 $$

The thermodynamic ionization constant in pure water, ${}^{w}K_A$, is related to the thermodynamic ionization constant in another medium by the definitional equation

$$ {}^{w}K_A = {}^{s}_{w}\gamma^{2}_{A} \; \hbar_A = {}^{s}_{w}\gamma^{2}_{oA} \; {}^{s}_{s}\gamma^{2}_{A} \; \hbar_A = {}^{s}_{w}\gamma^{2}_{oA} \; {}^{s}K_A \qquad \ldots.40 $$

in which

$$ {}^{s}_{w}\gamma^{2}_{A} = \frac{{}^{s}\gamma_H \; {}^{s}\gamma_R}{{}^{s}\gamma_{HR}}, \quad {}^{s}_{w}\gamma^{2}_{oA} = \frac{{}^{s}\gamma_{oH} \; {}^{s}\gamma_{oR}}{{}^{s}\gamma_{oHR}}, \quad {}^{s}_{s}\gamma^{2}_{A} = \frac{{}^{s}\gamma_H \; {}^{s}\gamma_R}{{}^{s}\gamma_{HR}} \quad \text{and} \quad \hbar_A = \frac{m_H \, m_R}{m_{HR}} . $$

In this case $\hbar_A$ represents values in the mixed solvent. In equation (40) the concentrations of the various species of the weak acid HR at equilibrium in the nonaqueous solvent (the value of $\hbar_A$ in the nonaqueous

solvent) are obtained and then the activity coefficients calculated which when multiplied by $\hbar_A$ will give the same value as ${}^{w}K_A$. This means that the standard state is taken to be in pure water. Making use of equation (39) and the fact that ${}^{s}K_A = {}^{s}\gamma_A^2 \hbar_A$ the various activity coefficients in equation (40) are obtained.

Equation (40) can now be written out in detail to aid in deducing the various factors involved in calculating the thermodynamic ionization constant of a weak acid in one solvent knowing the value in another solvent.

$$ {}^{w}K_A = \frac{{}^{s}\gamma_{oH}\ {}^{s}\gamma_{oR}}{{}^{s}\gamma_{oHR}} \cdot {}^{s}K_A \qquad \ldots.41 $$

Equation (40) indicates that the primary medium effect upon each of the various species must be known. It was thought that this result could be obtained directly from the hydrochloric acid data for a given mixed solvent, but at the present time it is not possible to obtain this result without further experimental work.

The relative partial molal heat content and relative partial molal heat capacity of an electrolyte can be calculated from galvanic cell data. The relative partial molal properties can be defined as the difference between the partial molal property in a given solution and its value in the reference state. The various relationships between the electromotive force of a cell and the relative partial molal quantities are derived in the following manner:

The relative free energy of one mole of solution is defined such that

$$ G - G^{o} = N_1(\bar{G}_1 - \bar{G}_1^{o}) + N_2(\bar{G}_2 - \bar{G}_2^{o}) + \ldots\ldots \qquad \ldots.42 $$

where N_1, N_2, N_i represent the respective mole fractions of the various components of the solution; $\bar{G}_i$ represents the partial molal free energy

of the ith component; and $\bar{G}_i^o$ represents the partial molal free energy in the standard state. In a similar manner the relative heat content per mole of solution can be represented by equation (43).

$$H - H^o = N_1(\bar{H}_1 - \bar{H}_1^o) + N_2(\bar{H}_2 - \bar{H}_2^o) + \ldots\ldots \quad \ldots.43$$

The activity of component i of a solution is defined so that equation (44) is valid.

$$\bar{G}_i = \bar{G}_i^o + RT \ln a_i \quad \ldots.44$$

Equation (42) can then be rewritten to give equation (45).

$$G - \bar{G}^o = N_1 RT \ln a_1 + N_2 RT \ln a_2 + \ldots\ldots \quad \ldots.45$$

Furthermore making use of the important thermodynamic relationship

$$\left[\frac{\partial(\frac{\Delta G}{T})}{\partial T}\right]_p = -\frac{\Delta H}{T^2} \quad \ldots.46$$

in which $\Delta G = G - \bar{G}^o$ and $\Delta H = H - H^o$ the following equation is obtained

$$\left[\frac{N_i\ \partial \ln a_1 + N_2\ \partial \ln a_2 + \ldots.}{\partial T}\right]_p = -\frac{N_1(\bar{H}_1 - \bar{H}_1^o) + N_2(\bar{H}_2 - \bar{H}_2^o) + \ldots.}{RT^2} \quad \ldots.47$$

This generalized equation is rarely used, instead it is more usual to limit the study to each component separately. Thus equation (47) can be expressed by equation (48).

$$\left[\frac{\partial(\ln a_i)}{\partial T}\right]_p = -\frac{(\bar{H}_i - \bar{H}_i^o)}{RT^2} \quad \ldots.48$$

The relative partial molal heat content of component i, $(\bar{H}_i - \bar{H}_i^o)$, is represented by $\bar{L}_i$ according to equation (49).

$$\bar{L}_i \equiv \bar{H}_i - \bar{H}_i^o \quad \ldots.49$$

Differentiation of equation (49) with respect to temperature at constant pressure serves to define another important quantity, the

relative partial molal heat capacity, $\bar{J}_i$.

$$\bar{J}_i \equiv \left[\frac{\partial \bar{L}_i}{\partial T}\right]_p = \bar{C}_{pi} - \bar{C}^o_{pi} = \left[\frac{\partial \bar{H}_i}{\partial T}\right]_p - \left[\frac{\partial \bar{H}^o_i}{\partial T}\right]_p \quad \ldots.50$$

The activity, a_2, of an electrolyte in solution can be expressed as the product of the mean activity coefficients and mean molalities of its ions as given by equations (8) and (9).

$$a_2 = (m_\pm \gamma_\pm)^\nu \quad \ldots.51$$

For electrolytes then equation (48) can be rewritten as

$$\bar{L}_2 = (\bar{H}_2 - \bar{H}^o_2) = -\nu RT^2 \left[\frac{\partial \ln \gamma_\pm m_\pm}{\partial T}\right]_p$$

and if m is held constant

$$\bar{L}_2 = (\bar{H}_2 - \bar{H}^o_2) = -\nu RT^2 \left[\frac{\partial \ln \gamma_\pm}{\partial T}\right]_{p,m} \quad \ldots.52$$

The electromotive force of the galvanic cell with hydrochloric acid as the electrolyte and an organic solvent and water as the medium was given by equation (27). If equation (27) is rearranged and solved for $\ln {}^s_s\gamma_\pm$, then it can be used in conjunction with equation (52) to show the relationship between the relative partial molal heat content and the electromotive force of a galvanic cell.

$$\bar{L}_2 = FT^2 \left[\frac{\partial \frac{({}^sE - {}^sE^o)}{T}}{\partial T}\right]_p \quad \ldots.53$$

This equation is commonly called the Gibbs-Helmholtz equation. After the appropriate differentiation, equation (53) reduces to equation (54).

$$\bar{L}_2 = FT \left[\frac{\partial({}^sE - {}^sE^o)}{\partial T}\right] - F({}^sE - {}^sE^o) \quad \ldots.54$$

Equation (54) indicates that the determination of the relative partial molal heat content of the electrolyte, hydrochloric acid, depends on the accuracy with which the temperature coefficient of the electromotive

force of the cell can be determined.

The relative partial molal heat capacity of the hydrochloric acid can also be determined from the electromotive force measurements. The relative partial molal heat capacity, $\bar{J}_2$, is defined in equation (50) as the derivative with respect to temperature at constant pressure of the relative partial molal heat content. Thus differentiating equation (54) with respect to temperature at constant pressure one obtains equation (55).

$$\bar{J}_2 = \left[\frac{\partial \bar{L}_2}{\partial T}\right]_p = FT\left[\frac{\partial^2(s_E - s_E^o)}{\partial T^2}\right] \quad \ldots.55$$

The next question of importance concerns the type of function that should be used to compute the variation of the electromotive force with temperature. As a first approximation it is assumed that the relative partial molal heat capacity, $\bar{J}_2$, varies linearly or

$$\bar{J}_2 = \bar{J}_{2(o)} + C'''(T-T_o) \quad \ldots.56$$

in which $\bar{J}_{2(o)}$ refers to some reference temperature, T_o, and C''' is a constant. If equation (55) is rearranged and integrated between the limits T_o and T equation (57) is obtained.

$$\int_{T_o}^{T} d\bar{L}_2 = \int_{T_o}^{T} \bar{J}_2 \, dT = \bar{L}_2 - \bar{L}_{2(o)} \quad \ldots.57$$

Substituting equation (56) for $\bar{J}_2$ in equation (57)

$$\bar{L}_2 = L_{2(o)} + \left[\int_{T_o}^{T} (\bar{J}_{2(o)} + C''' T - C''' T_o) dT\right]$$

and performing the integration gives the equation (58).

$$\bar{L}_2 = a'' + b''T + c''T^2 \quad \ldots.58$$

in which

$$a'' = \bar{L}_{2(o)} - \bar{J}_{2(o)} T_o + \frac{C''' T_o^2}{2}$$

$$b'' = \bar{J}_{2(o)} - C'''T_o$$

and

$$c'' = \frac{C'''}{2}$$

Substituting equation (58) into equation (53) gives

$$\frac{\partial}{\partial T}\left(\frac{{}^{s}E - {}^{s}E^{o}}{T}\right) = \frac{1}{FT^2}\left[a'' + b''T + c''T^2\right]$$

or

$${}^{s}E - {}^{s}E^{o} = \frac{1}{F}\left[- a'' + b''T \ln T + c''T^2 + IT\right] \quad \ldots\ldots 59$$

in which I is an integration constant.

For work in which the electromotive force measurements are known with accuracy greater than ±0.05 millivolts and the temperature range is greater than $40^{o}C$, ${}^{s}E$ and ${}^{s}E^{o}$ may be expressed as

$${}^{s}E = a' + b'T + c'T^2 + d' T \ln T$$

$${}^{s}E^{o} = a'_o + b'_oT + c'_oT^2 + d'_oT \ln T$$

However it has been found (3) over a limited temperature range, (0^{o} - $35^{o}C$), ${}^{s}E$ and ${}^{s}E^{o}$ can be expressed to within ±0.05 millivolts by the following quadratic equation.

$${}^{s}E = a + bT + dT^2 \quad \ldots\ldots 60$$

$${}^{s}E^{o} = a_o + b_oT + d_oT^2 \quad \ldots\ldots 61$$

It appears within a limited temperature range the logarithmic term can be dropped from the original equations.

If the electromotive forces of a cell are given by equations (60) and (61) then $\bar{L}_2$ from equation (54) becomes

$$\bar{L}_2 = -F[(a-a_o) - (c-c_o)T^2] \quad \ldots\ldots 62$$

Similarly from equation (55) J_2 becomes

$$\bar{J}_2 = 2F(c - c_o)T \qquad \ldots.63$$

The coefficients of equations (60) and (61) can be determined quite easily by using the method of least squares on the electromotive force data of the same cell at various temperatures. The actual procedure will be discussed in a later section of this work.

In order to carry out some of the calculations described in the previous discussion it is necessary to have accurate values of E^o. It was pointed out that equation (23) provided a means of obtaining E^o by extrapolation to zero molality. However, the nonlinearity of such a plot leads to some degree of error. As was also pointed out, there are equations which can be used which give more nearly linear plots, but unfortunately values of the dielectric constants of the solvent systems are needed. To get the most accuracy out of plots involving equation (23) it was decided to use a curve fitting technique making use of the IBM 1620 computer. The technique will be described in more detail in a later section. The program is based on the assumption that a set of experimental data can be fitted to a polynomial of the form:

$$y = A_o + A_1x + A_2x^2 + \ldots. A_{15}x^{15} \qquad \ldots.64$$

In practice the quantity $[E + \frac{2RT}{F} \ln m]$ was taken as the ordinate while the square root of the molality was taken as the abcissa. Then by using equation (64) it was assumed that

$$E + \frac{2RT}{F} \ln m = A_o + A_1 m^{1/2} + A_2m + A_3m^{3/2} \ldots. \qquad \ldots.65$$

If this assumption is correct, E^o can be obtained by setting the molality equal to zero.

To show how the use of equation (65) can be justified from a theoretical point of view one must consider equation (23) again.

$$E + \frac{2RT}{F} \ln m = E^{o} - \frac{2RT}{F} \ln \gamma_{\pm} \quad \ldots.23$$

If it can be shown that $\ln \gamma_{\pm}$ can be expressed by a series equation in $m^{1/2}$, then substitution of this equation into equation (23) will give a new equation which is an analogue of equation (65).

Derivation of an equation for $\ln \gamma_{\pm}$ has been carried out by Debye and Hückel (3). The assumptions of the Debye-Hückel theory may be stated in the following manner (11, 28):

1) Strong electrolytes are assumed to be completely dissociated in solution.

2) The closest distance of approach of two ions,"a", is the same for all ions in solution.

3) For the purpose of calculating the electrostatic potential of an individual ion, the charges on all other ions may be replaced by a continuous charge distribution, which fills the space outside the distance of closest approach, is spherically symmetrical, and has a density determined by Boltzmann's statistical law.

4) The potential satisfies Poisson's equation, in which the dielectric constant of the solution is assumed to be that of the pure solvent.

5) At the distance of closest approach to an individual ion, the potential and field strength are the same as for a point charge equal to the charge of the ion in question and placed at its center.

Using these assumptions Debye and Hückel set up their fundamental differential equation now generally known as the Poisson-Boltzmann

equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = -\frac{4\pi\epsilon}{D}\sum_{j=1}^{s}\frac{Nn_jz_j}{V}\exp\left(-\frac{z_i\epsilon\psi_i}{\kappa T}\right) \quad \ldots.66$$

in which ψ_i represents the electrostatic potential due to an ion of the ith kind at a distance r from that ion; ϵ represents the unit electric charge and $z_j\epsilon$ the charge on the jth ion; D represents the dielectric constant of the pure solvent; N is Avogadro's number; κ is the Boltzmann constant; V is the volume of the solution which contains n_o moles of solvent and n_i moles of the ion of the ith kind; and T represents the absolute temperature.

The boundary conditions for ψ_i follow:

1) As $r \to \infty$, $\psi_i \to 0$.

2) $\frac{d\psi_i}{dr} = \frac{\epsilon z_i}{D}\cdot\frac{1}{a_i^2}$ for $r = a_i$. This simply states that the medium is uniform and continuous throughout.

Assuming the electrolytes are completely dissociated in solutions one considers all deviations from ideality to be the consequence of electrostatic interactions between the ions (5). It is then necessary to calculate the extra free energy arising from these interactions and then relate this extra free energy to the activity coefficient. The extra free energy due to electrostatic interaction can be calculated in the following manner. Imagine that a given ion is introduced into a solution in the uncharged state. A negligible amount of electrical energy is required for this process. Now imagine the charge to be increased gradually up to the full charge of the ion. Electrical energy is required to charge the ion and the amount can be expressed by equation (67).

$$\Delta G_{j(elec.)} = \int_o^{z_j\epsilon}\psi_i\, de_j \quad \ldots..67$$

in which $z_j\epsilon$ and e_j represent the charge on the jth ion.
The activity coefficient can be related to the free energy change by equation (68).

$$\bar{G} = \bar{G}^{o} + \nu RT \ln a_{\pm} = \bar{G}^{o} + \nu RT \ln \gamma_{\pm} m_{\pm} = \bar{G}^{o} + \nu RT \ln \gamma_{\pm} + \nu RT \ln m_{\pm} \quad ....68$$

The free energy change can be divided into two parts:

$$\bar{G}_m = \bar{G}^{o} + \nu RT \ln m_{\pm} \quad ....69$$

$$\bar{G}_\gamma = \nu RT \ln \gamma_{\pm} \quad ....70$$

Equation (69) is of the form of the limiting law for dilution solutions of un-ionized solutes and would presumably apply to solutions of electrolytes as well were it not for the charges on the ions. Therefore it is assumed, for completely ionized electrolytes in dilute solutions, that the deviation of electrolytes solutions from ideality can be attributed entirely to electrostatic forces between the ions. This is equivalent to identifying $\bar{G}_\gamma$ with $N\Delta G_{(elec.)}$.

The problem now becomes one of finding the correct expression for ψ_i, or of solving equation (66). It is at this point Debye and Hückel made their simplifying approximation. They assumed that in solvents of high dielectric constant the exponential term can be approximated as

$$\exp\left(-\frac{z_j\epsilon\psi_i}{kT}\right) \simeq 1 - \frac{z_j\epsilon\psi_i}{kT} \quad ....71$$

This comes from the first two terms of the expansion of the exponential function. However, in solvents of lower dielectric constant such as were used in the studies described later, this approximation is not valid. Consequently, the higher terms of the exponential expansion must be included.

Consider an electrolyte at a concentration of n moles per volume V

which dissociates into two kinds of ions. The summation term in equation (66) becomes

$$\sum_{1}^{2} \frac{Nn_j z_j \epsilon}{V} \exp\left(-\frac{z_j \epsilon \psi_i}{kT}\right) = \frac{\nu_1 Nnz_1 \epsilon}{V} \exp\left(-\frac{z_1 \epsilon \psi_i}{kT}\right) + \frac{\nu_2 Nnz_2 \epsilon}{V} \exp\left(-\frac{z_2 \epsilon \psi_i}{kT}\right) \quad \ldots.72$$

in which ν_1 and ν_2 represent the number of cations and anions resulting from the dissociation of one molecule of electrolyte. Now $\nu_1 z_1 \epsilon = -\nu_2 z_2 \epsilon$ and if $z_1 \epsilon$ is equal to $-z_2 \epsilon$, as in the case of a symmetrical electrolyte, equation (72) reduces to equation (73).

$$\sum_{1}^{2} \frac{Nn_j z_j \epsilon}{V} \exp\left(-\frac{z_j \epsilon \psi_i}{kT}\right) = \frac{\nu_1 Nnz_1 \epsilon}{V} \left[\exp\left(-\frac{z_1 \epsilon \psi_i}{kT}\right) - \exp\left(\frac{z_1 \epsilon \psi_i}{kT}\right)\right] \quad \ldots.73$$

The bracketed part of equation (73) is twice the hyperbolic sine of $\frac{z_1 \epsilon \psi_i}{kT}$ and consequently the summation is given by equation (74).

$$-\frac{2\nu_1 Nnz_1 \epsilon}{V} \left[\frac{z_1 \epsilon \psi_i}{kT} + \frac{1}{3!}\left(\frac{z_1 \epsilon \psi_i}{kT}\right)^3 + \frac{1}{5!}\left(\frac{z_1 \epsilon \psi_i}{kT}\right)^5 + \ldots.\right] \quad \ldots.74$$

It is apparent then that for symmetrical types of electrolytes the Debye and Hückel approximation has neglected the effects of the third, fifth and higher odd-numbered orders. Furthermore, it is also apparent that for unsymmetrical electrolytes, terms of the even as well as odd-numbered orders must be considered.

Substitution of equation (74) for the summation term in equation (66) yields the differential equation which must be solved. Further simplification can be made when the case of hydrochloric acid is considered since ν_1 and z_1 are both unity.

Gronwall, LaMer, and Sandved have treated this problem solving equation (66) for the symmetrical electrolyte case (11). Later the unsymmetrical case was studied also (28). For the symmetrical case

the following expression was obtained for the logarithm of the mean activity coefficient:

$$\ln \gamma_{\pm} = - \frac{(\epsilon z)^2}{2D\mathfrak{k}T} \frac{\kappa}{1+\kappa a} + \left[\frac{(\epsilon z)^2}{D\mathfrak{k}Ta}\right]^3 [\tfrac{1}{2}X_3(\kappa a) - 2Y_3(\kappa a)] + \left[\frac{(\epsilon z)^2}{D\mathfrak{k}Ta}\right]^5 [\tfrac{1}{2}X_5(\kappa a) - 4Y_5(\kappa a)] \quad \ldots.75$$

in which a is the average minimum distance of approach of the ions and $\kappa^2 = \frac{8\pi N\epsilon^2 n z^2}{\mathfrak{k}TDV}$ in which N is Avogadro's number and n is the number of moles of electrolyte in volume V. The first term on the right hand side of equation (75) is identical with the Debye-Hückel equation for $\ln \gamma_{\pm}$ and represents the first approximation (3). The next two terms represent the contribution of the third and fifth order terms. The quantities $X_3(\kappa a)$, $Y_3(\kappa a)$, $X_5(\kappa a)$, and $Y_5(\kappa a)$ are complicated series functions of κa, and have been obtained by Gronwall, LaMer and Sandved (11).

From the work of Gronwall, LaMer and Sandved the following expressions have been obtained:

$$X_3 = - \frac{1}{6} \frac{x^2}{(1+x)^4} [1 - 4xe^{4x}E(4x)] \quad \ldots.76$$

in which $x = \kappa a$, $E(x) = \int_x^{\infty} \frac{e^{-u}}{u} du$, $E(\alpha x) = \int_x^{\infty} \frac{e^{-\alpha u}}{u} du$;

$$Y_3 = - \frac{f_1(x) - e^{4x} E(4x) f_2(x)}{6(1+x)^4} \quad \ldots.77$$

in which $f_1(x) = \sum_{n=2}^{\infty} a_n x^n$ and $f_2(x) = \sum_{n=3}^{\infty} b_n x^n$;

$$X_5 = \frac{x^5}{120(1+x)^6} \left[- \frac{1}{3x^3} + \frac{1}{x^2} + \frac{14}{x} - \frac{10}{1+x} - 24e^{6x} E(6x) - \frac{80}{1+x} e^{4x}E(4x) - \frac{80(1-x)}{(1+x)} e^{8x} E(4x)^2 + 80e^{6x} \int_x^{\infty} \frac{e^{-2u}E(4u)\, du}{u} \right] \quad \ldots.78;$$

and

$$Y_5 = \frac{1}{120(1+x)^7}\left[f_1(x) + f_2(x)\, e^{4x}E(4x) + f_3(x)e^{8x}E(4x)^2 + f_4(x)e^{6x} \left[\int_x^\infty \frac{e^{-2u}E(4u)\,du}{u} - \frac{3}{10}E(6x)\right]\right] \quad \ldots.79$$

in which $f_1(x) = \sum_{n=2}^{\infty} a_n x^n$, $f_2(x) = \sum_{n=5}^{\infty} b_n x^n$, $f_3(x) = \sum_{n=5}^{\infty} c_n x^n$, and $f_4(x) = \sum_{n=5}^{\infty} d_n x^n$.

Consider the first term of the right hand side of equation (75). The fraction $\frac{\varkappa}{1+\varkappa a}$ can be expressed as

$$\frac{\varkappa}{1+\varkappa a} = \varkappa - \varkappa^2 a + \varkappa^3 a^2 - \varkappa^4 a^3 + \varkappa^5 a^4 \ldots. \quad \ldots.80$$

Notice also that the quantity $(\frac{ez}{2D\hbar T})^2$ is a constant under the condition of constant temperature.

Now consider the higher ordered terms of equation (75). First consider X_3 from equation (76). $E(4x)$ is represented by

$$E(4x) = \int_x^\infty \frac{e^{-4u}}{u}\,du \quad \ldots.81$$

The solution of such an integral is of the form

$$E(4x) = \log\frac{1}{x} - C - \sum_{\nu=1}^{\infty} \frac{(-4)^\nu x^\nu}{\nu!\,\nu} \quad \ldots.82$$

in which C is the Euler constant (11). The quantity $\log\frac{1}{x}$ can be expressed in series form. Furthermore, e^{4x} can be expanded to give

$$e^{4x} = 1 + 4x + \frac{16x^2}{2!} + \frac{64x^3}{3!} + \ldots. \quad \ldots.83$$

and the fraction $\frac{x^2}{(1+x)^4}$ can be expressed as a series similar to equation (80). The net result is that all the terms of equation (76) can be expressed as a series or a product of several series, and consequently

the X_3 term may be expressed as a series in x itself simply by combining the various series it is composed of.

Turning next to equation (77) or the Y_3 term, $f_1(x)$ and $f_2(x)$ have been defined as series and e^{4x} and $E(4x)$ have been shown to be series expressions. Upon division by $(1 + x)^4$ therefore Y_3 can also be expressed in a series in x.

Although the fifth order terms X_5 and Y_5 are more complicated than X_3 and Y_3 they also can be expressed in a series in x using the same arguments as used for X_3 and Y_3.

Upon combination of all these series, equation (75) may be expressed in a series in κ and x. Recalling that $x = \kappa a$ equation (75) then becomes a series in κ

$$\ln \gamma_{\pm} = A''\kappa + B''\kappa^2 + C''\kappa^3 + D''\kappa^4 + \ldots . \qquad \ldots .84$$

in which the constants are determined by combining the various series involved.

Recalling that κ^2 is proportional to the number of moles of electrolyte and hence the molality, equation (84) becomes

$$\ln \gamma_{\pm} = A' m^{1/2} + B'm + C'm^{3/2} + \ldots . \qquad \ldots .85$$

Substitution of equation (85) for the expression $\ln \gamma_{\pm}$ in equation (23) yields

$$E + \frac{2RT}{F} \ln m = E^{o} + Am^{1/2} + Bm + Cm^{3/2} + \ldots . \qquad \ldots .86$$

which is of the same form as equation (65). Thus it has been shown that using the higher terms of Debye-Hückel theory one can obtain an equation for the expression $E + \frac{2RT}{F} \ln m$ which is an analogue to the equation obtained by using the curve fitting program.

CHAPTER III

EXPERIMENTAL PROCEDURE

The following cell was studied at four different temperatures and with five different compositions of solvent:

$$H_2(1\ atm.) \mid HCl(m)\ Monoglyme\ (Y),\ Water\ (X) \mid Ag\ Cl\text{-}Ag$$

In addition some work was done with acetonitrile as the organic component.

The basic cell design is shown in figure 1. Two hydrogen electrodes and two silver-silver chloride electrodes were used in each cell, therefore making it possible to take a total of four readings for each solution by interchanging electrode pairs. The electromotive force of each cell was measured by means of a Leeds and Northrup K-3 type potentiometer set up according to the instructions given in the manual accompanying the instrument. A sensitive Rubicon galvanometer and an Eppley low temperature coefficient standard cell were used in conjunction with the potentiometer.

Three Sargent Thermoniter controlled water baths with a precision regulation to $\pm 0.01^{\circ}C$ and equivalent uniformity were used in conjunction with a Sargent water bath cooler to give temperature baths of 15°, 25°, and $35^{\circ}C$. A fourth temperature bath was made by placing ice and water in a convenient container; in this case a small styrofoam ice chest. The temperature of the cell solution was checked in the various baths and agreement was within $0.1^{\circ}C$ in all except the $0^{\circ}C$ case. In the case of $0^{\circ}C$ the solution temperature was higher than $0^{\circ}C$ by as much as $0.7^{\circ}C$.

The hydrogen electrodes were prepared from Sargent half cell platinum electrodes (S--30505) of a length of 125 mm (1). The

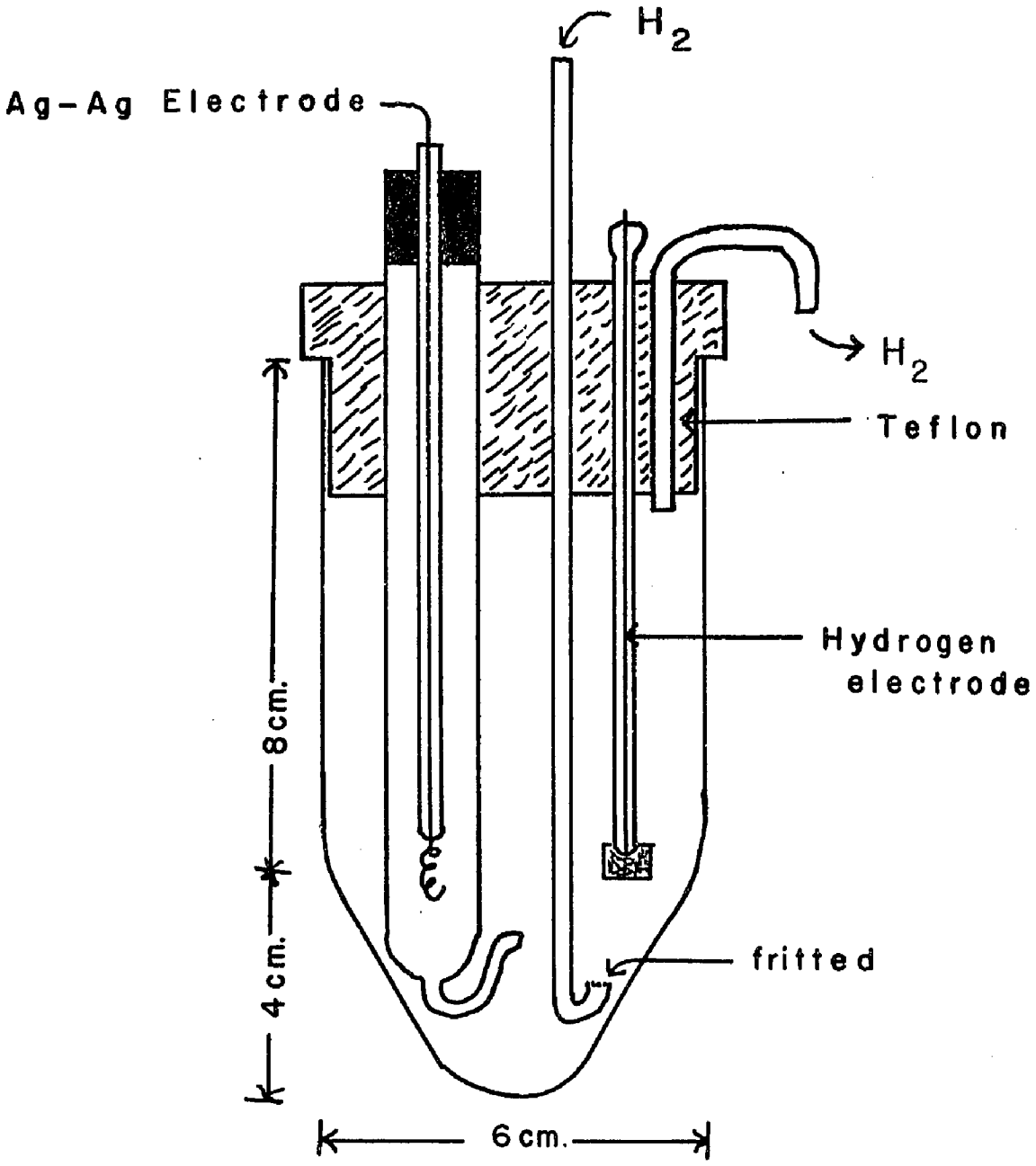
H2
Ag–Ag Electrode
H2
Teflon
Hydrogen
electrode
8cm.
4cm.
fritted
6cm.

FIGURE I

electrodes were cleaned by immersing them briefly in a solution prepared by combining three volumes of 12M hydrochloric acid with one volume of 16M nitric acid and four volumes of distilled water. The electrodes were rinsed thoroughly with distilled water and then placed in a platinic acid solution for plating. The platinic acid solution was prepared in the following way.

One and one-half grams of scrap platinum were cleaned in hot concentrated nitric acid, rinsed with distilled water and ignited in a Bunsen flame. The metal was cut into small fragments to facilitate solution and then was digested in warm aqua regia until dissolved. The acid mixture was evaporated to dryness over a steam bath and the residue was dissolved in 20 ml. of concentrated hydrochloric acid. The evaporation and addition of concentrated hydrochloric acid was repeated twice. The residue, chloroplatinic acid hexahydrate, $H_2PtCl_6 \cdot 6H_2O$, remaining after a fourth evaporation was dissolved in 100 ml. of distilled water, and 80 mg. of lead acetate trihydrate was added. The solution was then stored in a glass stoppered bottle.

A current of 100 ma. was passed for three or four minutes in such a direction that the electrode to be coated was the cathode while another platinum electrode served as the anode. The current is not critical, but when smaller currents were used, the time required to properly coat the electrode was increased. The criterion for good electrodes was a uniform, nonstreaking, black coat. Although the coating can be quite heavy it was found the lighter coatings were better since the platinum black did not fall off so easily. The lifetime of the electrodes was several months.

Various other types of hydrogen electrodes were used. These included: a lightly platinized electrode, the coating of which was a light gray color; a platinum electrode which had no platinum black coating; a platinum electrode prepared by polishing the platinum foil with the end of a stirring rod on a glass plate, then treating it with warm aqua regia and then concentrated nitric acid, and finally washing it with distilled water (10); and last of all, a suspension electrode similar to that of Hills and Ives (26).

Several black hydrogen electrodes were prepared, and the potentials were intercompared in a dilute aqueous hydrochloric acid solution. Agreement to ±0.1 millvolts was considered adequate for this work, however, several electrodes differed in the hundreds of millivolt range. If an electrode did not agree with the others within ±0.1 millivolts, it was discarded.

The silver-silver chloride electrodes were prepared by a method adapted from Bates (1). The base for the electrode was a helix of number 26 platinum or silver wire approximately seven mm. in length and two mm. in diameter, sealed in a tube of flint glass. The bases were cleaned in warm 6N nitric acid and then rinsed with distilled water. A thin paste of well-washed silver oxide, prepared in the manner described below, was applied to each electrode base. The electrodes were then placed in an oven with a temperature of 500°C until the paste turned white. This normally took ten minutes although no particular attention was given to the heating time. This process was repeated until each base had four layers of dried silver oxide on it.

The silver oxide solution was prepared according to Bates (1). 338 grams of silver nitrate were dissolved in three liters of distilled water. Then sodium hydroxide solution was added drop wise to the vigorously stirred silver nitrate solution. The silver oxide precipitate which formed was washed at least once a day for a period of one month with distilled water. The silver oxide was then stored with distilled water in a glass stoppered bottle and kept in the dark.

The electrodes were then electrolyzed as anodes in a 1M solution of twice distilled hydrochloric acid for 45 minutes at a current of 10 ma. with a platinum electrode as the cathode. The electrodes were then placed in 0.005 M hydrochloric acid overnight and then stored in distilled water. The potentials were intercompared in a dilute aqueous hydrochloric acid solution and those electrodes whose potentials differed from the average by more than 0.1 millivolt were rejected. The color of the electrodes was light gray. Out of thirteen electrodes three were found suitable for use.

Distilled water was obtained by distilling distilled water from a permanganate solution through a column of glass beads 18 inches high and two and one-half inches in diameter. All connections were glass. The resulting distillate had a conductivity of less than 1×10^{-6} reciprocal ohms. Whenever distilled water was used it was obtained in the above manner.

Monoglyme was purified from the bulk supply obtained from Ansul Company, Menominee, Wisconsin. Sodium wire was added to the bulk monoglyme and the solution was shaken. The solution was then allowed

to sit for several days over the sodium. The monoglyme was then refluxed with powdered lithium aluminum hydride overnight and distilled off through an eight foot heated column. The distillation apparatus was equipped with an automatic magnetic shut off so approximately eighty percent of the condensed vapor was returned to the distillation pot. In addition a nitrogen sweep was employed so collection of the monoglyme was accomplished in a nitrogen atmosphere. The first 40-50 ml. of distillate were discarded as well as the last fraction. Due to the nitrogen atmosphere the boiling point of the monoglyme was slightly higher than the literature value, but throughout the middle fraction of distillate the temperature remained at a constant value.

Acetonitrile was purified in the following manner (8). It was first shaken with potassium hydroxide pellets and allowed to sit for 24 hours. Approximately 100 grams of potassium hydroxide was used per 500 grams of acetonitrile. The acetonitrile was then kept over anhydrous sodium carbonate for several days. It was then distilled from drierite through a three foot heated column; only the middle fraction was kept. The distillate then was saturated with dry nitrogen and stored in a nitrogen atmosphere.

The hydrochloric acid stock solution was prepared from reagent-grade acid which had been distilled twice in an all-glass still. Each time only the middle fraction was kept. The acid was then diluted with distilled water to make an approximate 1N stock solution. The stock solution was standardized gravimetrically as silver chloride by means of a method adapted from Vogel (7) and also volumetrically

with sodium carbonate (7).

All solutions used for electromotive force studies were made volumetrically from the stock hydrochloric acid solution, solvents and distilled water. The concentrations were converted to the weight scale with the use of the appropriate density data. This procedure should make the acid concentration valid to within 0.4% of the given values. No volumes were determined by difference, that is by using a volumetric flask and diluting to the calibration line, but rather the volume of each solvent or solution was measured individually.

The hydrogen gas used for these studies was Matheson ultra pure hydrogen. The hydrogen was further purified by passing it through a Deoxo catalytic purifier. Before entering the cell the hydrogen was then saturated with the cell solution by passing it through a bubbler containing the cell solution.

It was found that a small frit was necessary to insure proper saturation of the cell solutions with hydrogen. In addition the hydrogen was allowed to leave the cell through a short piece of rubber tubing. The use of these adaptations enabled a steady state to be reached. Previous to their use much difficulty was experienced in attaining a steady state in the system.

The general procedure in obtaining the electromotive force data was to turn on the hydrogen gas and allow the cell to equilibrate. A steady state was assumed to be reached when successive readings taken at one-half hour intervals varied by ±0.1 millivolts or less. It was found that a steady state was reached in two to three hours for the 10 and 20 percent monoglyme solutions and that it was reached

more quickly at higher temperatures.

While the electromotive force was observed over a period of time, occasionally the hydrogen flow rate was changed, either by by-passing the cell or by actually changing the flow rate. If a steady state was attained, very little change in the electromotive force was observed when the hydrogen flow rate was changed.

Two solvent systems were studied, the monoglyme-water system and the aceonitrile-water system. The monoglyme-water system was studied at five different compositions, 8.68, 17.81, 46.52, 67.03 and 88.80 percent monoglyme. Ten solutions of varying hydrochloric acid concentrations ranging from 0.1 molal to 0.001 molal were studied in each solvent system. Acetonitrile-water mixtures of 10, 20, 50, 75 and 90 volume percent were studied at 25°C; the 10 percent by volume solutions were also studied at 0° and 35°C. As indicated previously, satisfactory results were not obtained.

It was found that the electromotive force measurements became increasingly difficult to make as the acid concentration became smaller and the composition became more concentrated in the organic solvent. In the more concentrated hydrochloric acid solutions the galvanometer deflection during the actual reading was large, and as a result the null point could be identified quite easily. However, as the concentration of hydrochloric acid decreased and the composition of organic solvent increased, the null point became more difficult to determine.

The reproducibility of the electromotive measurements of the various cells depended upon the composition of the mixed solvent; generally greater organic solvent composition resulted in poorer

reproducibility. Several methods were used to check the reproducibility. Frequently after a cell had been measured at all four temperatures, it was returned to former temperatures to check on hysteresis. In addition several cell solutions were prepared again and the electromotive forces were measured at the various temperatures.

The electromotive forces of the solutions in which the monoglyme composition was 8.68 percent were reproducible to tenth of millivolts place and in some cases to 0.1 millivolts.

The solutions in which the monoglyme composition was 17.81 percent were reproducible to the same degree as the 8.68 percent monoglyme solutions. A series of 17.81 percent monoglyme solutions was studied by the author four months previous to this work and agreed in the tenths of millivolt range and even to ±0.1 millivolts with the present work. In addition, solutions returned to a former temperature gave results within 0.3 millivolts of the original results, even after the rough handling involved in transferring the cell back and forth between the various temperature baths.

Re-investigation of the 46.52 percent series showed a deviation slightly greater than that in the 17.81 percent series. This was noticeable to a greater extent at 35°C than at the lower temperatures.

Reproducibility was much more difficult in the 67.03 and 88.80 percent compositions of monoglyme. This lack of reproducibility was not due to the lack of a steady state at the hydrogen electrode because the electromotive force did not change substantially with a change in hydrogen flow rate. It was felt that the lack of reproducibility was due to the loss of the more volatile solvent. Several times a cell solution was saturated with hydrogen overnight, but when the cell was

returned to the same temperature later, a higher electromotive force was observed. This phenomena was observed to a greater degree after the cell had been at one of the higher temperatures. In addition, observation of the data from all monoglyme systems showed that the electromotive force of cells with about the same hydrochloric acid concentration was higher in solutions containing the lower percentages of monoglyme. It is on the basis of this observation and the fact that the electromotive force of the 67.03 and 88.80 percent cells increased that loss of monoglyme is suggested as the cause for the poor reproducibility. The differences in electromotive force readings when a cell was returned to a former temperature appeared in the millivolt range for the 67.03 percent system and were even more pronouned in the 88.80 percent system.

As indicated previously, some work was carried on in acetonitrile-water solutions. Two facts indicate that a steady state at the hydrogen electrode was not achieved in these studies. First, a steady galvanometer reading was never observed. Second, a change in the flow rate of hydrogen resulted in a change in the electromotive force of the cell. A technique which involved by-passing the cell with the hydrogen and then taking the electromotive force one minute later was tried. As the calculated results show, this was not satisfactory. The general trend seemed to be to higher electromotive force values as the hydrochloric acid decreased. This can be explained by the hydrolysis of the acetonitrile with the hydrochloric acid. The reason for the greater deviation at lower concentration of hydrochloric acid is that the acid consumed in the hydrolysis is negligible when compared with the more concentrated solutions but is not negligible

compared with the more dilute solutions of hydrochloric acid. From equation (27) it is obvious if m is small the electromotive force is higher.

CHAPTER IV

DATA AND RESULTS

All calculations except those of the primary medium effect were carried out with the IBM 1620 computer. Each individual program was checked out by carrying out several long hand calculations.

The first program provided the means for calculating from the laboratory data the quantities given in Tables I through VI. The molality, m, in terms of the number of moles of hydrochloric acid per kilogram of mixed solvent was calculated from the volumetric data and the appropriate density data. The density data for water and acetonitrile was obtained from the Hand Book of Chemistry and Physics while the density of monoglyme was obtained from a technical data sheet furnished by Ansul Chemical Company, the manufacturers. The procedure was to calculate the total number of grams of organic solvent, the total number of grams of water and the number of moles of hydrochloric acid. The molality then was simply the number of moles of acid times one thousand divided by the sum of the grams of organic solvent and grams of water.

The quantity labeled E_{obs} corresponds to the electromotive force of the particular cell when the partial pressure of hydrogen gas is one atmosphere. This means that the electromotive forces obtained directly from the cells have been corrected by addition of a correction increment obtained from equation (20). The correction was obtained in the following manner: The barometric pressure was recorded when each electromotive force was measured. Equation (20) indicates that the vapor pressure of the solvent is needed since the partial pressure of hydrogen will be the difference between the

barometric pressure and the vapor pressure of the solvent according to Dalton's Law. Normally when the solvent is a pure substance such as water, the vapor pressure is easily obtained, but when there are two components as in these studies the vapor pressure of the solvent is a composite pressure. If it is assumed that Raoult's Law is valid,then the vapor pressures of each component are calculated from their respective mole fractions and the vapor pressure of the pure substances. The sum of these vapor pressures constitutes the vapor pressure of the solvent according to Dalton's Law. Some workers have made further correction terms considering the depth of the hydrogen jet in the solution and also the vapor pressure lowering effect of the hydrochloric acid upon the mixed solvent. It was felt that these corrections were not necessary in these studies for the reason that the electromotive force values were known only to the tenths of millivolts place. These corrections would be noticed in the hundredths of millivolts place. The vapor pressure data used for the various calculations is given in Table A-5 in the appendix. The source of the monoglyme vapor pressures was the technical data sheet furnished by Ansul. The water vapor pressures were obtained from the Hand Book of Chemistry and Physics, while the vapor pressures of acetonitrile were taken from Jordon (4).

The quantity $E + \frac{2RT}{F}$ in m is represented in Tables I through VI by E log m. This quantity is on the left hand side of equation (23) and is used in extrapolating to obtain the values of E°. This quantity is calculated by adding the quantity $\frac{2RT}{F}$ ln m to the appropriate values of E_{obs}. As previously indicated a plot of the quantity $E + \frac{2RT}{F}$ ln m versus some function of the molality can be used to obtain E° by

TABLE I

VALUES OF m, E_{obs} AND $E_{obs} + \frac{2RT}{F} \ln m$ FOR 8.68 PERCENT MONOGLYME-WATER MIXTURES AT 0°, 15°, 25° AND 35°C.

	0°C		15°C		25°C		35°C	
m	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm
.09732	.34944	.23979	.34909	.23341	.34809	.22840	.34584	.22214
.07783	.35934	.23917	.35969	.23292	.35929	.22812	.35694	.22137
.05835	.37211	.23838	.37310	.23203	.37292	.22695	.37158	.22072
.03888	.38978	.23695	.39162	.23040	.39192	.22510	.39117	.21876
.01944	.41978	.23431	.42372	.22807	.42563	.22319	.42631	.21707
.00972	.45098	.23288	.45624	.22616	.45895	.22089	.46019	.21414
.00777	.46090	.23229	.46705	.22589	.46995	.22042	.47141	.21351
.00583	.47297	.23083	.48062	.22518	.48413	.21982	.48628	.21310
.00389	.49209	.23086	.49991	.22433	.50405	.21891	.50718	.21247
.00194	.52402	.23016	.53365	.22366	.53925	.21850	.54341	.21190

TABLE II

VALUES OF m, E_{obs} AND $E_{obs} + \frac{2RT}{F} \ln m$ FOR 17.81 PERCENT MONOGLYME-WATER MIXTURES AT 0°, 15°, 25° AND 35°C.

	0°C		15°C		25°C		35°C	
m	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm
.09976	.34429	.23580	.34311	.22867	.34112	.22270	.33808	.21569
.07978	.35439	.23538	.35383	.22829	.35212	.22222	.34948	.21522
.05981	.36659	.23402	.36671	.22687	.36560	.22090	.36346	.21391
.03885	.38481	.23194	.38625	.22498	.38595	.21909	.38478	.21233
.01942	.41562	.23011	.41836	.22267	.41916	.21668	.41936	.21008
.00971	.44689	.22874	.45123	.22111	.45302	.21491	.45378	.20768
.00777	.45657	.22792	.46141	.22021			.46498	.20703
.00582	.47002	.22779	.47568	.22015	.47803	.21364	.47969	.20643
.00388	.48839	.22709	.49501	.21937	.49830	.21309	.50016	.20539
.00198	.51887	.22602	.52700	.21807	.53120	.21155	.53446	.20409

TABLE III

VALUES OF m, E_{obs} AND $E_{obs} + \frac{2RT}{F} \ln m$ FOR 46.52 PERCENT MONOGLYME-WATER MIXTURES AT 0°, 15°, 25° AND 35°C.

	0°C		15°C		25°C		35°C	
m	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm
.10425	.33134	.22493	.32410	.21184	.31873	.20258	.31233	.19229
.08326	.34127	.22427	.33425	.21083	.32858	.20088	.32239	.19040
.06245	.35307	.22254	.34636	.20866	.34140	.19892	.33550	.18824
.04160	.36921	.21955	.36388	.20600	.35941	.19606	.35422	.18539
.02080	.39899	.21671	.39486	.20258	.39140	.19244	.38700	.18137
.01040	.42679	.21190	.42436	.19767	.42180	.18724	.41830	.17588
.00828	.43945	.21381	.43723	.19920	.43466	.18837	.43284	.17830
.00624	.45107	.21209	.44968	.19758	.44841	.18756	.44621	.17661
.00417	.46810	.21022	.46787	.19582	.46689	.18541	.46549	.17457
.00208	.49955	.20888	.50101	.19438	.50094	.18367	.50034	.17243

TABLE IV

VALUES OF m, E_{obs} AND $E_{obs} + \frac{2RT}{F} \ln m$ FOR 67.03 PERCENT MONOGLYME-WATER MIXTURES AT 0°, 15°, 25° AND 35°C.

	0°C		15°C		25°C		35°C	
m	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm
.10728	.30592	.20086	.29353	.18269	.28465	.16997	.27426	.15574
.08579	.31461	.19902	.30261	.18068	.29423	.16807	.28439	.15400
.06432	.32521	.19607	.31351	.17728	.30538	.16442	.29653	.15084
.04282	.34143	.19314	.33073	.17430	.32260	.16074	.31395	.14666
.02141	.36501	.18410	.35531	.16447	.34992	.15245	.34203	.13794
.01069	.39248	.17887	.38378	.15844	.37915	.14599	.37201	.13103
.00856	.40191	.17786	.39421	.15786	.38854	.14398	.38144	.12869
.00642	.41390	.17627	.40661	.15593	.40129	.14191	.39506	.12698
.00428	.43113	.17446	.42475	.15398	.41983	.13966	.41315	.12358
.00214	.46110	.17178	.45541	.15020	.45124	.13544	.44616	.11977

TABLE V

VALUES OF m, E_{obs} AND $E_{obs} + \frac{2RT}{F} \ln m$ FOR 88.80 PERCENT MONOGLYME-WATER MIXTURES AT 0°, 15°, 25° AND 35°C.

	0°C		15°C		25°C		35°C	
m	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm	Eobs	Elogm
.11055	.23086	.12720	.20775	.09840	.19661	.08347	.18310	.06617
.08840	.23773	.12355	.21431	.09387	.20838	.08375	.19007	.06126
.06627	.24515	.11742	.22345	.08870	.21159	.07217	.19809	.05399
.04416	.25806	.11122	.23595	.08104	.22511	.06484	.21021	.04456
.02207	.27764	.09815	.25563	.06629	.24530	.04939	.23151	.02903
.01103	.29781	.08570	.27412	.05035	.26509	.03357	.25290	.01361
.00883	.30498	.08236	.28113	.04629	.27349	.03050	.25851	.00737
.00662	.31088	.07472	.29346	.04433	.28142	.02365	.26751	.00109
.00441	.32549	.07024	.30428	.03502	.29740	.01879	.28236	-.00559
.00221	.34462	.05675	.32441	.02073	.31527	.00105	.30238	-.02238

TABLE VI

VALUES OF m, E_{obs} AND $E_{obs} + \frac{2RT}{F} \ln m$ FOR 10 PERCENT BY VOLUME ACETONITRILE-WATER MIXTURES AT 0° and 35° C.

	0°C		35°C	
	Eobs	Elogm	Eobs	Elogm
.10602	.32853	.22291	.25264	.13349
.07568	.34203	.22055	.26748	.13042
.04237	.36607	.21728	.30481	.13696
.03025	.38317	.21851	.31929	.13354
.01058	.43148	.21741	.37332	.13181
.00756	.45689	.22697	.39719	.13781
.00302	.49611	.22306	.45153	.14349
.00178	.54472	.24668		

extrapolation. Any graphic extrapolation involves a high degree of error particularly when carried out along a curved portion of the plot. To make such plots as accurate as possible a curve fitting technique was used to carry out the extrapolations.

The revised version of the IBM 7.0.002 polynomial curve fitting program was used to carry out the extrapolations. This program is based on the assumption that a set of experimental data can be fitted to a polynomial of the form:

$$y = A_o + A_1x + A_2x^2 + A_3x^3 + \ldots\ldots A_{15}x^{15} \qquad \ldots\ldots 64$$

The justification of the empirical equation has been discussed in a previous section of this work. The linear form, $y = A_o + A_1x$, is tried as a first approximation. The coefficients (A's) are computed and the standard error of the dependent variable y is compared to a predetermined maximum tolerance. If the error is greater than the maximum tolerance, the process is repeated, adding a term of the form A_nx^n (where n = 2, 3, 4, ... 15) until the error is within the tolerance. In each case the coefficients are computed by the least squares technique. A modified Gaussian elimination technique is used to solve the resulting set of linear equations. The program also permits the optional use of weight factors. Instead of designating the maximum tolerance or in addition to the maximum tolerance the highest order of polynomial fitted may be designated. In these cases the repetitive process is stopped when either the maximum tolerance is reached or the highest polynomial previously designated is reached.

For the extrapolations the quantity $E + \frac{2RT}{F} \ln m$ was taken as the abcissa or dependent variable while $m^{1/2}$ was taken as the ordinate or independent variable. No maximum tolerance was designated and the third degree was the highest polynomial fitted. For each degree the coefficients were calculated, $E + \frac{2RT}{F} \ln m$ computed for each vlaue of $m^{1/2}$, the difference between the observed and computed values of $E + \frac{2RT}{F} \ln m$ obtained, and the standard error given. As a result, three sets of coefficients were given for each extrapolation.

The decision as to what set of coefficients or what equation to use for extrapolation purposes was made by taking into account the standard error and the general shape of a rough curve of the experimental data. The experimental points were first plotted versus $m^{1/2}$. Then the values calculated from the various equations were plotted versus $m^{1/2}$. In each case, it was not difficult to eliminate two of the equations. It was really not necessary to consider the first degree equation as the plot always had a slight curvature. In general, the third degree equation had greatest curvature and in the systems of low monoglyme concentration tended to take the experimental points at low acid concentration into greater account. This, of course, would be unwise since these values are of less certainty than those corresponding to higher hydrochloric acid concentration.

The coefficients of the equations used for extrapolation purposes are given in Table VII for each system and temperature. The standard error for each equation is also given. It was not necessary to use the third degree equation except for the systems having the highest

TABLE VII

COEFFICIENTS OF THE EMPIRICAL EQUATION

$$E_{obs} + \frac{2RT}{F} \ln m = A + Bm^{1/2} + Cm + Dm^{3/2}$$

FOR MONOGLYME-WATER MIXTURES

x = 8.68

t°C	A	B x 10^2	C x 10^2	D	Standard Error
0	0.22721	6.2099	-6.8714	0	0.00034
15	0.22089	6.1487	-6.6973	0	0.00015
25	0.21550	6.2737	-6.6091	0	0.00026
35	0.20889	6.1159	-5.8003	0	0.00031

x = 17.81

t°C	A	B x 10^2	C x 10^2	D	Standard Error
0	0.22415	4.7565	-3.1670	0	0.00025
15	0.21581	5.7221	-5.0184	0	0.00025
25	0.20903	6.5241	-6.8383	0	0.00020
35	0.20092	7.8325	-9.9941	0	0.00014

x = 46.52

t°C	A	B x 10^2	C x 10^2	D	Standard Error
0	0.20488	9.3269	-9.4175	0	0.00081
15	0.19017	9.6545	-8.9622	0	0.00069
25	0.17948	9.9162	-8.5895	0	0.00069
35	0.16855	9.8629	-7.8517	0	0.00097

TABLE VII (Cont.)

x = 67.03

$t^{o}C$	A	B x 10^2	C x 10^2	D	Standard Error
0	0.16368	17.1834	-17.4850	0	0.00075
15	0.14161	19.3381	-20.5225	0	0.00082
25	0.12604	21.9664	-26.1580	0	0.00031
35	0.10907	24.4020	-30.9891	0	0.00025

x = 88.80

$t^{o}C$	A	B x 10^2	C x 10^2	D	Standard Error
0	0.02502	81.4613	-261.2843	3.2842	0.00121
15	-0.01125	82.6044	-244.5720	2.8735	0.00171
25	-0.03095	84.9331	-246.6216	2.8993	0.00270
35	-0.06039	97.9980	-308.1550	3.8657	0.00135

monoglyme concentration.

The graphical plots of the experimental values are given in figures 2 through 6. The experimental points were first placed on the graphs and then the curve corresponding to the appropriate equation was drawn. The curves correspond to the equations obtained through the curve fitting technique.

The values of E^o obtained through the curve fitting program are given in Table VIII. All numbers given in the previous tables are those numbers taken directly from the computer. These values should be corrected to within the limits of error of the experimental data. However, since these values were used in subsequent calculations, no corrections were made until the final quantities were obtained. One of the objects of this work was to determine the E^o values and consequently these values have been rounded off to the fourth place. This is not meant to imply, however, that the E^o values are known to within ±0.1mv. The limits of error and accuracy of the extrapolations will be discussed in Chapter 5. The E^o values for the aqueous system were obtained from Harned and Owen (3).

Table IX gives the coefficients of an equation of the form:

$$E^o = a_o + b_oT + c_oT^2 \qquad \ldots.61$$

in which T represents the absolute temperature in degrees Kelvin. This particular set of equations is necessary for calculations to obtain the relative partial molal heat content and the relative partial molal heat capacity. The curve fitting technique was used to obtain the coefficients. Since only four temperatures were used in the study, only four observations could be used in determining the equation coefficients.

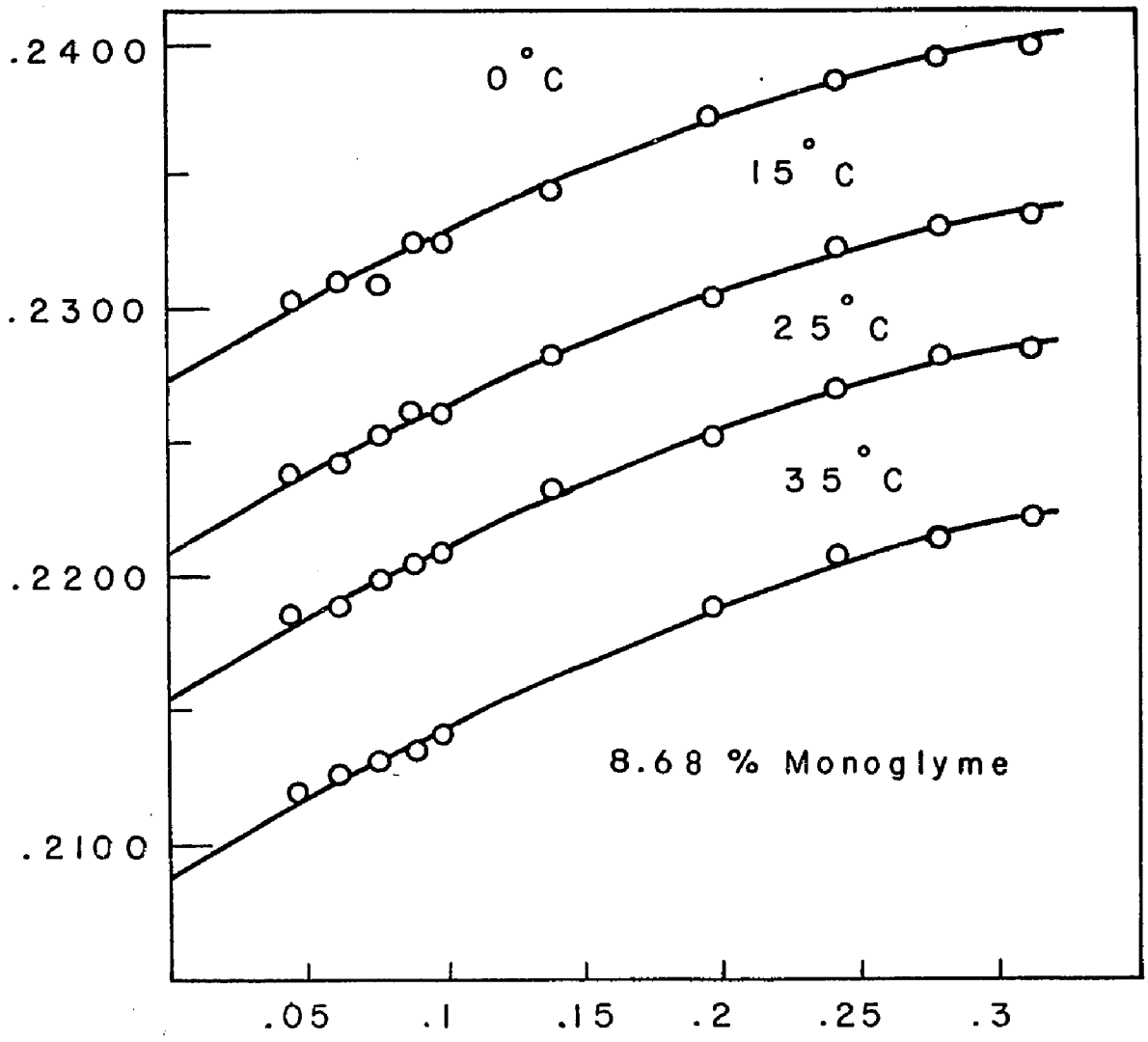

Figure 2

$E_{obs} + \frac{2RT}{F} \ln m$ Versus $m^{1/2}$

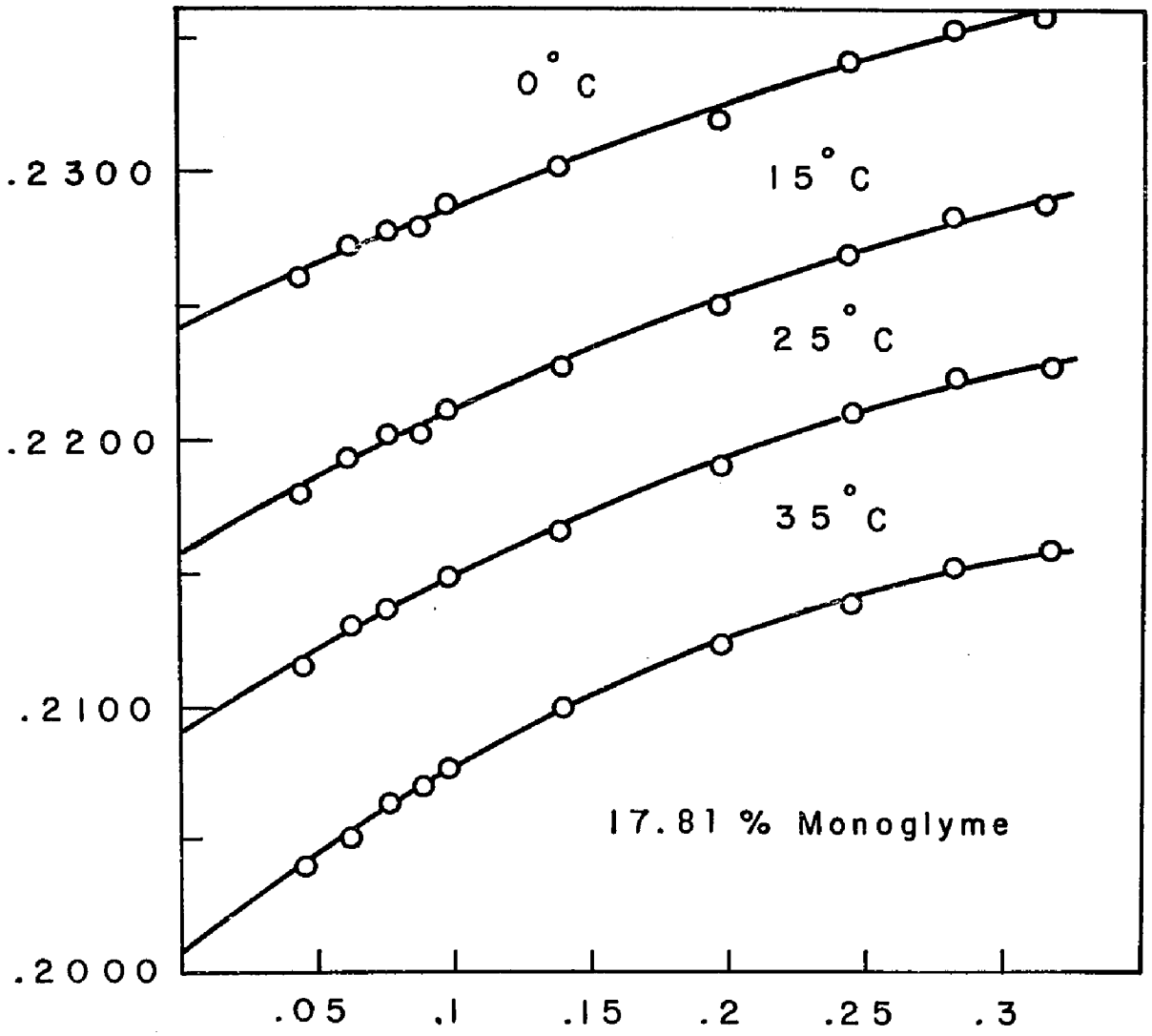

Figure 3

$E_{obs} + \frac{2RT}{F} \ln m$ Versus $m^{1/2}$

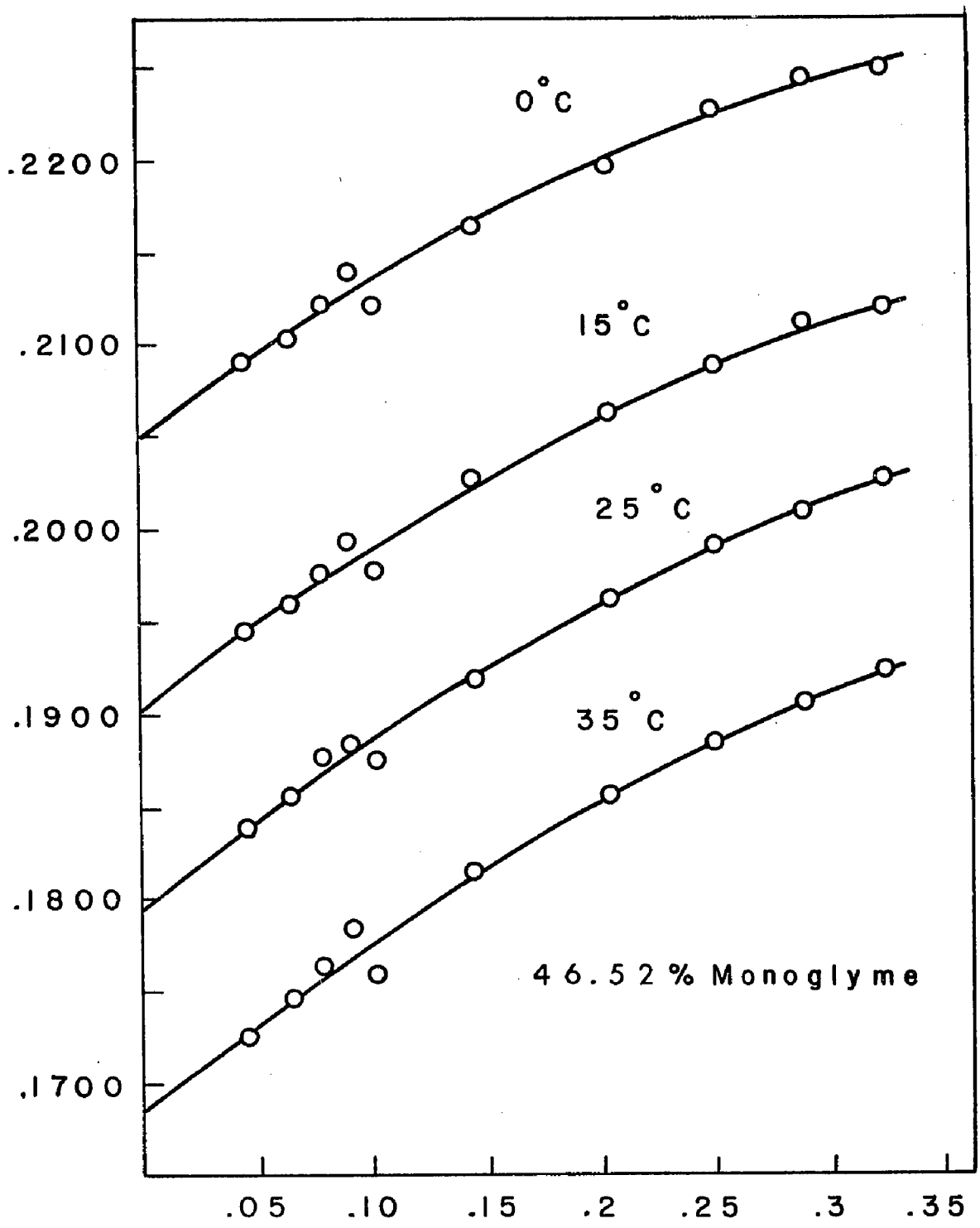

Figure 4

$E_{obs} + \frac{2RT}{F} \ln m$ Versus $m^{1/2}$

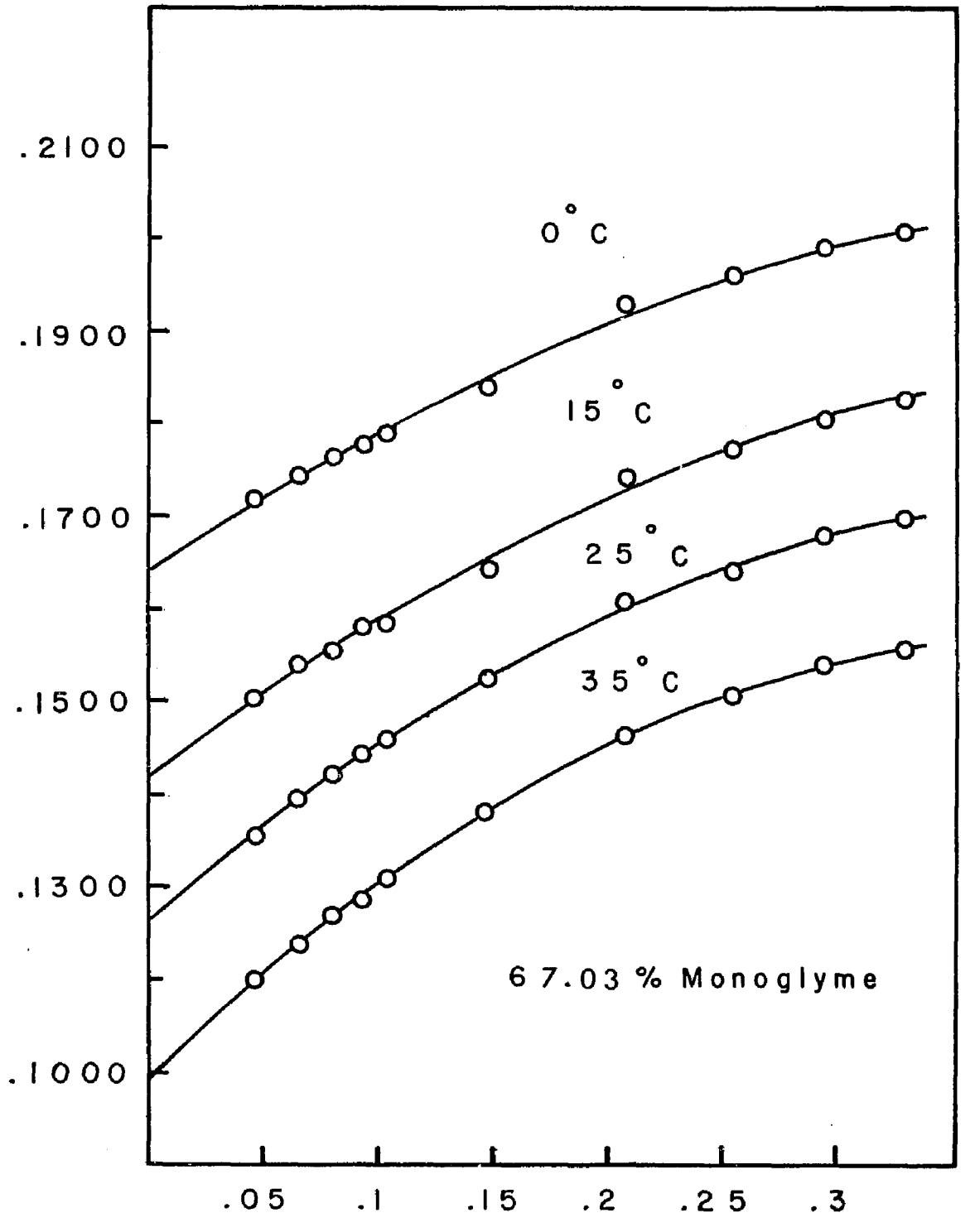

Figure 5

$E_{obs} + \frac{2RT}{F}$ ln m Versus $m^{1/2}$

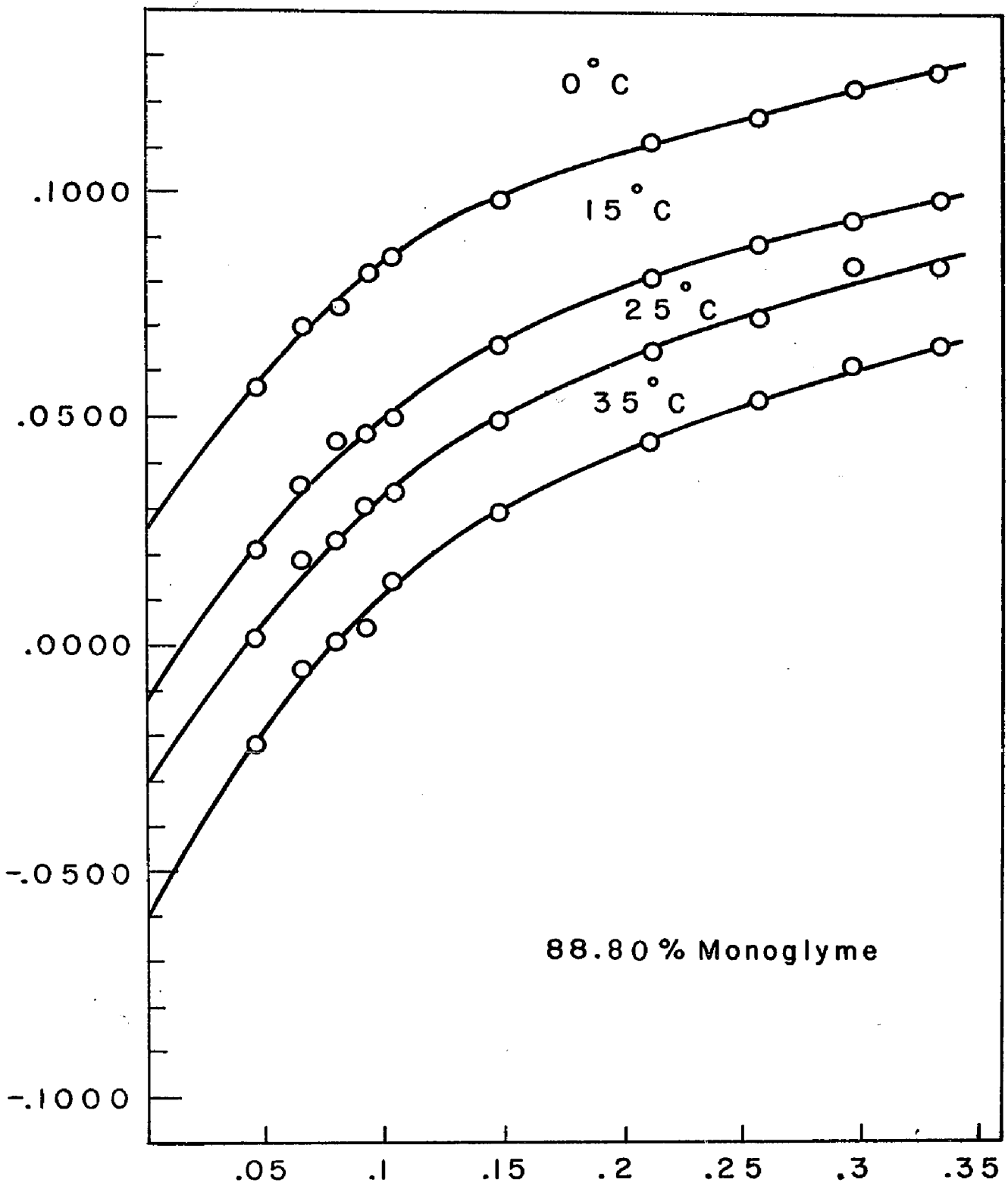

Figure 6

$E_{obs} + \frac{2RT}{F} \ln m$ Versus $m^{1/2}$

TABLE VIII

E^{o} VALUES

x = percent monoglyme

x	0^{o}	15^{o}	25^{o}	35^{o}
0	0.23655	0.22857	0.22234	0.21565
8.68	0.2272	0.2209	0.2155	0.2089
17.81	0.2242	0.2158	0.2090	0.2009
46.52	0.2049	0.1902	0.1795	0.1685
67.03	0.1637	0.1416	0.1260	0.1091
88.80	0.0250	-0.0113	-0.0310	-0.0604

TABLE IX

COEFFICIENTS OF EMPIRICAL EQUATION $E^o = a_o + b_o T + c_o T^2$

x = percent monoglyme

x	$a_o \times 10^2$	$b_o \times 10^3$	$c_o \times 10^6$	Standard Error
8.68	- 7.1611	2.5268	-5.2456	0.00007
17.81	- 6.3271	2.5722	-5.5648	0.00009
46.52	26.7372	0.4899	-2.6308	0.00012
67.03	18.4475	1.2374	-4.8089	0.00018
88.47	24.5295	.5945	-5.1363	0.00426

The mean activity coefficients of hydrochloric acid are given in Table X. The values corresponding to x = 0, or the aqueous system were taken from Harned and Owen (3). The values for the aqueous system contain the proper number of significant figures. The values for the mean activity coefficients in the various mixed solvent systems correspond to ${}^{s}_{s}\gamma_{\pm}$, that is they are referred to the infinitely dilute state in the mixed solvent. The values were obtained in the following manner: The equation used for extrapolation purposes, the coefficients of which are given in Table VII, was used to obtain the value of $E + \frac{2RT}{F} \ln m$ at rounded concentrations. The mean activity coefficients were then calculated from an equation resulting from the rearrangement of equation (23). That is

$$\ln \gamma_{\pm} = \frac{E^{o} - (E + \frac{2RT}{F} \ln m)}{\frac{2RT}{F}} \qquad \ldots.87$$

The values given in Table X were taken directly from the computer. In Chapter V the correction for the proper number of significant figures will be discussed and applied for each system.

The primary medium effect as defined by Owen in equation (31) was calculated by means of the same equation. The E^{o} values used for the calculations are those given in Table VIII. The values of the primary medium effect for each system at four temperatures are given in Table XI.

The secondary medium effects for given concentrations of hydrochloric acid were calculated from the values of the mean activity coefficients of monoglyme-water mixtures and the values given for

TABLE X

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN MONOGLYME-WATER MIXTURES AT 0°, 15°, 25° AND 35°C.

x = 0

m	0°	15°	25°	35°
.1	.8027	.8000	.7964	.7918
.05	.8346	.8329	.8304	.8265
.02	.8774	.8770	.8755	.8731
.01	.9065	.9055	.9048	.9025
.005	.9303	.9297	.9285	.9268
.002	.9541	.9530	.9521	.9513
.001	.9668	.9661	.9656	.9647

x = 8.68

m	0°	15°	25°	35°
.1	.762434	.773578	.772959	.774911
.05	.800890	.811013	.811602	.816325
.02	.854367	.862294	.863316	.868447
.01	.889281	.895519	.896501	.900990
.005	.917597	.922356	.923190	.926829
.002	.945458	.948678	.949290	.951869
.001	.960536	.962893	.963357	.965285

TABLE X (Cont.)

x = 17.81

m	0°	15°	25°	35°
.1	.777016	.768455	.764539	.757101
.05	.825031	.812885	.804597	.789985
.02	.878566	.866953	.858151	.842844
.01	.909980	.900198	.892540	.879244
.005	.934170	.926409	.920219	.909466
.002	.957097	.951687	.947308	.939689
.001	.969199	.965187	.961916	.956221

x = 46.52

m	0°	15°	25°	35°
.1	.652744	.647653	.641982	.644336
.05	.709588	.708538	.706089	.710757
.02	.786444	.787499	.786992	.792056
.01	.836810	.838282	.838363	.842848
.005	.877989	.879438	.879740	.883419
.002	.918860	.920028	.920371	.923010
.001	.941138	.942061	.942361	.944346

TABLE X (Cont.)

x = 67.03

m	0°	15°	25°	35°
.1	.457020	.441169	.430431	.419083
.05	.532259	.514659	.495829	.479104
.02	.642736	.626159	.604797	.586713
.01	.720403	.705990	.686143	.669504
.005	.786954	.775116	.758138	.743942
.002	.855692	.847116	.834403	.823774
.001	.894279	.887778	.877988	.869796

x = 88.80

m	0°	15°	25°	35°
.1	.119026	.114699	.109467	.096798
.05	.153415	.148923	.145515	.130135
.02	.215500	.216236	.214903	.191023
.01	.287816	.292580	.292398	.262341
.005	.378719	.386508	.387145	.353227
.002	.512092	.521679	.522883	.488777
.001	.610168	.619595	.620899	.589831

TABLE XI

PRIMARY MEDIUM EFFECTS OF MONOGLYME-WATER MIXTURES UPON HYDROCHLORIC ACID. COMPUTED FROM EQUATION (31).

x = weight percent of monoglyme

x	0°	15°	25°	35°
8.68	0.086	0.067	0.058	0.055
17.81	0.114	0.112	0.113	0.121
46.52	0.292	0.336	0.362	0.385
67.03	0.672	0.761	0.814	0.872
88.80	1.952	2.097	2.141	2.257

TABLE XII

VALUES OF THE SECONDARY MEDIUM EFFECT OF MONOGLYME-WATER MIXTURES UPON HYDROCHLORIC ACID. COMPUTED FROM EQUATION (36).

x = weight percent of monoglyme

x = 8.68

m	0°	15°	25°	35°
.1	-.022347	-.014583	-.012973	-.009362
.05	-.017902	-.011563	-.009942	-.005379
.02	-.011551	-.007343	-.006085	-.002320
.01	-.008327	-.004813	-.004001	-.000727
.005	-.005970	-.003444	-.002490	.000014
.002	-.003951	-.001974	-.001283	.000260
.001	-.002822	-.001444	-.001010	.000263

x = 17.81

m	0°	15°	25°	35°
.1	-.014121	-.017468	-.017728	-.019458
.05	-.005007	-.010562	-.013706	-.019621
.02	.000577	-.005003	-.008691	-.015314
.01	.001664	-.002550	-.005924	-.011336
.005	.001803	-.001540	-.003890	-.008198
.002	.001362	-.000599	-.002191	-.005333
.001	..001076	-.000411	-.001660	-.003833

TABLE XII (Cont.)

x = 46.52

m	0°	15°	25°	35°
.1	-.089794	-.091731	-.093591	-.089487
.05	-.070459	-.070217	-.070415	-.065510
.02	-.047521	-.046741	-.046277	-.042301
.01	-.034735	-.033492	-.033114	-.029693
.005	-.025130	-.024133	-.023423	-.020816
.002	-.016342	-.015289	-.014717	-.013109
.001	-.011681	-.010941	-.010578	-.009259

x = 67.03

m	0°	15°	25°	35°
.100000	-.244574	-.258438	-.267180	-.276265
.050000	-.195320	-.209035	-.223915	-.236770
.020000	-.135141	-.146288	-.160618	-.172607
.010000	-.099774	-.108070	-.120116	-.129671
.005000	-.072661	-.078962	-.088018	-.095430
.002000	-.047268	-.051141	-.057297	-.062498
.001000	-.033858	-.036711	-.041302	-.044967

TABLE XII (Cont.)

x = 88.80

m	0°	15°	25°	35°
.100000	-.828761	-.843377	-.861694	-.912587
.050000	-.735477	-.747495	-.756244	-.802704
.020000	-.609641	-.607962	-.609905	-.659859
.010000	-.498164	-.490555	-.490489	-.536484
.005000	-.390235	-.381116	-.379840	-.418857
.002000	-.270197	-.261642	-.260231	-.289155
.001000	-.199851	-.192880	-.191742	-.213626

hydrochloric acid in the aqueous system. The secondary medium effects were calculated with the use of equation (36).

In order to calculate the relative partial molal quantities, $\bar{L}_2$ and $\bar{J}_2$, it was necessary to express the electromotive forces in the form of equation (60). This was done by means of the curve fitting program described previously. Selected molalities were chosen and the electromotive forces of these cells were fitted versus the absolute temperature. The coefficients of the equation are given in Table XIII.

With the coefficients given in Tables IX and XIII the relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacity, $\bar{J}_2$, were calculated at selected molalities and at each temperature. All calculations were carried out on the computer.

TABLE XIII

COEFFICIENTS OF THE EMPIRICAL EQUATION $E_{obs} = a + bT + cT^2$ FOR MONOGLYME-WATER MIXTURES

x = weight percent of monoglyme

x = 8.86

m	a x 10^3	b x 10^3	c x 10^6	Standard Error
0.0973	4.78846	2.46756	-4.41348	0.00022
.0584	-26.00587	2.76564	-4.79195	.00022
.00972	-68.14381	3.33762	-5.26455	.00016
.00583	-68.37941	3.41998	-5.25558	.00014
.001940	-70.79956	3.61504	-5.26736	.00011

x = 17.81

m	a x 10^3	b x 10^3	c x 10^6	Standard Error
0.0998	-48.63281	2.87771	-5.26620	0.000007
.0598	- 1.04734	2.60920	-4.62672	.00001
.00971	3.74812	2.87903	-4.60378	.00002
.00582	- 5.89601	3.03809	-4.74655	.00002
.001980	-28.72703	3.38924	-5.06638	.00005

TABLE XIII (Cont.)

x = 46.52

m	a x 10^3	b x 10^3	c x 10^6	Standard Error
0.1043	198.30267	1.40919	-3.37285	0.00009
.01040	232.07911	1.56055	-3.08316	.00003
.00417	244.05359	1.62303	-2.93502	.00008
.002080	251.15262	1.68652	-2.84430	.00008

x = 67.03

m	a x 10^3	b x 10^3	c x 10^6	Standard Error
0.1073	192.53901	1.59412	-4.31202	0.00013
.0428	323.47256	0.77958	-2.63276	.00039
.01069	309.10158	1.11348	-2.95021	.00039
.00428	276.69864	1.50541	-3.44594	.00034
.002140	252.99455	1.79682	-3.79671	.00030

TABLE XIII (Cont.)

x = 88.80

m	a x 10^3	b x 10^3	c x 10^6	Standard Error
0.1106	1004.39490	-4.16252	4.87370	0.00265
.0442	823.08418	-2.73212	2.42630	.00222
.01103	1039.18310	-3.99535	4.68487	.00207
.00441	1563.85440	-7.58186	11.13502	.00122
.002210	222.04616	1.95542	-5.50708	.00344

TABLE XIV

VALUES OF THE RELATIVE PARTIAL MOLAL QUANTITIES, $\bar{L}_2$ AND $\bar{J}_2$. CALCULATED FROM EQUATIONS (62) and (63).

x = 17.81

	0°		15°		25°		35°	
	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$
.0598	165	12	346	12	472	13	602	13
.00971	106	12	293	13	423	13	557	14
.00582	71	10	228	11	337	11	451	12
.001980	47	6	142	7	208	7	276	7

x = 67.03

	0°		15°		25°		35°	
	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$
.0428	546	27	969	29	1264	30	1569	31
.01069	327	23	688	25	939	26	1199	26
.00428	213	17	478	18	661	19	852	19
.002140	158	13	354	13	491	14	632	14

CHAPTER V

DISCUSSION AND CONCLUSIONS

The molalities of the various solutions were calculated from the volumetric data and the appropriate densities. For all mixed solvent systems except perhaps the 67.03 and 88.80 percent monoglyme mixtures, it seems reasonable to expect a maximum error of 0.4 percent or four parts per thousand. Great care was taken in the preparation of the solutions so this value would seem to be high and a better estimate is 0.1 to 0.2 percent. In the 67.03 and 88.80 percent monoglyme, the error is about 0.3 percent.

The experimental values for the electromotive forces of the cells have errors which vary with the particular system studied. The 8.68 and 17.81 percent monoglyme-water systems had the least error of all systems. The error in the electromotive force values is estimated to be ±0.1 millivolt on the basis of the reproducibility of the cells and the fact that the criteria for a steady state was that readings taken over a half hour period varied by 0.1 millivolts or less. In each system the criterion for a steady state was the same but the reproducibility varied. The error for 46.52 percent monoglyme mixtures would be estimated at ±0.5 millivolts. In 67.03 and 88.80 percent monoglyme the errors in the electromotive force values are estimated to be ±0.8 millivolts and ± several millivolts, respectively.

An examination of Tables I through VI shows that in each system and at every temperature a decrease in the molality results in a corresponding increase in the value of E_{obs}. In addition, for cells of

approximately the same acid concentration an increase in the monoglyme composition results in a decrease in E_{obs} values. There seems to be no regular trend in the E_{obs} values with a change temperature except when given molalities of given solvent systems are considered.

The quantity $E_{obs} + \frac{2RT}{F} \ln m$ decreases with decreasing acid concentration, and at the same acid concentration decreases with increasing temperature.

Table VI gives the data obtained from cells containing 10 percent by volume acetonitrile. The behavior of this system is irregular. Rather than a decrease in the values of $E_{obs} + \frac{2RT}{F} \ln m$ with decreasing acid concentration, there is at first a slight decrease but then at the lower acid concentrations there is an increase. In the monoglyme systems, the decrease is consistent and according to theory this should be the case also in the acetonitrile-water systems. This peculiarity plus the fact that a satisfactory equilibrium condition was not attained at the hydrogen electrode in acetonitrile-water mixtures suggests that some process that uses hydrogen ion is taking place. To see how this might be the case notice again the following: The E_{obs} values increase with decreasing acid concentration. Furthermore, the term $\frac{2RT}{F} \ln m$ is negative enough to cause the quantity $E_{obs} + \frac{2RT}{F} \ln m$ to decrease with decreasing molality. The electromotive force of a cell is given by equation (22).

$$E_{obs} = E^{o} - \frac{2RT}{F} \ln \gamma_{\pm} m \qquad \ldots.22$$

A molality which is actually less than the value expected would result in a higher E_{obs} value than expected. In dilute solutions, $\gamma_{\pm}$ will

not change appreciably. A high value of E_{obs} would result in a high $E_{obs} + \frac{2RT}{F} \ln m$ value. It would seem then at low concentrations that the molality is actually much smaller than it is. This would be the result if hydrogen ion were being used up by some process. The puzzling question, however, is why aren't the higher concentrations affected. One possible answer is that the process itself is slow and uses up only a small fraction of the hydrogen ions available in the concentrated acid solutions. In the dilute acid concentrations, the fraction used is no longer small and greatly reduces the hydrogen ion concentration in solution, resulting in high E_{obs} values and high $E_{obs} + \frac{2RT}{F} \ln m$ values.

In surveying possible chemical reactions which might occur between acetonitrile and hydrogen ions, it was found that one possibility was the hydrolysis of the acetonitrile to an amide or even to an acid. One indication of a reaction was the dependence of the higher $E_{obs} + \frac{2RT}{F} \ln m$ values upon both the acetonitrile composition and the temperature. Since the hydrogen electrode is so sensitive to hydrogen ion, one interesting extension of this work would be the study of the kinetics of the process. Presently some preliminary work is being done to determine the products resulting from the process.

The error encountered in E^o is a composite error consisting of errors from at least two sources. The first source is in the values of the quantity $E_{obs} + \frac{2RT}{F} \ln m$. The second source is in the actual extrapolation process.

Consider the first source of error. The errors in transforming the values of the measured electromotive force to values corresponding

to a hydrogen partial pressure of one atmosphere result from making several assumptions concerning the behavior of the mixed solvent. Since changes between E_{obs} values and the original electromotive force values occurred mainly in the hundredths of millivolts place, it would seem any error made by assuming the ideal behavior of the solvent system would be negligible or outside the actual error in the measurements. An error of 0.2 percent in the molality would give an error of about 0.0001 in the $\frac{2RT}{F}$ ln m term. The maximum error then in the $E_{obs} + \frac{2RT}{F}$ ln m term would be 0.2 millivolts for the 8.68 and 17.81 percent monoglyme systems. For the 46.52 percent solutions, the error in the $E_{obs} + \frac{2RT}{F}$ ln m term would be approximately 0.4 millivolts, for 67.03 percent solutions about 1.0 millivolts and for the 88.80 percent solutions several millivolts.

The error brought about through the actual extrapolation process is difficult to assess at the present time. A comparison of the extrapolations used in other studies with the extrapolations used in this study would be very helpful but is unavailable. It is hoped that such a comparison can be made in the near future. A few observations will give some insight into the problem of the error in the extrapolation process. An examination of figures 2 through 6 shows that with increasing monoglyme composition the curvature of the plot becomes more pronounced. Any graphical extrapolation along a curved plot is subject to a high degree of error. In addition to this fact, the experimental points corresponding to the lowest molalities or more dilute acid solutions are experimentally the

most uncertain measurements of all. As was noted previously, these were the most difficult measurements to make and with greater monoglyme concentration the difficulty increased. Thus in extrapolations of this kind great care must be taken. To eliminate as much of the graphical extrapolation error as possible, the method of least squares was used to find an equation which corresponded to the experimental data.

It would seem at this time that the greatest source of error found in the E^o values can be attributed to the error in the $E_{obs} + \frac{2RT}{F} \ln m$ values. In Table VII, the E^o values have been rounded to the tenths of millivolt place. For the values corresponding to monoglyme compositions of 8.68 and 17.81 percent, the error in E^o would be about ±0.2 millivolts, for 46.52 percent about ±1.0 millivolts and for 88.80 ± several millivolts.

Before discussing other results it will be well to consider what has been done to the general study of mixed solvents by electromotive force methods with the use of the curve fitting program for extrapolation purposes. Most of the mixed solvent systems studied by the electromotive force method have been those systems, the dielectric constants of which have been previously determined. In the process of finding a suitable solvent system for carrying out chemical reactions, one does not necessarily restrict himself to the limited number of systems, the dielectric constants of which have been determined. Consequently, it is of considerable value to be able to study the thermodynamics of hydrochloric acid in systems for which dielectric constants are not known. It has been shown that the

curve fitting technique allows such studies to be carried out with elimination of some of the error previously encountered in graphical extrapolations.

It will be of benefit to discuss the equations whose coefficients are given in Table XIII. As has already been mentioned in Chapter II in discussing the relative partial molal quantities, an equation of the form

$$E = a + bT + cT^2 \qquad \ldots.60$$

is useful for the calculation of these quantities. Cells with selected molalities were chosen for the study of the relationship between the electromotive force and absolute temperature of the cell. The E_{obs} values used for this study were those corresponding to the $E_{obs} + \frac{2RT}{F} \ln m$ values calculated from the equations used for extrapolation purposes. Since the cells were studied at only four temperatures, only four points were available for curve fitting. An error in any one of these data could result in an equation differing greatly from the actual equation. Harned and coworkers (12-25) have studied cells at 5^{o} intervals over a rather wide temperature range. With a larger number of temperatures, an error in one point would not cause as serious error as when only four points are used.

Table V in Chapter IV contains the actual values of the mean activity coefficients of hydrochloric acid in monoglyme-water mixtures as calculated from the empirical equations used for extrapolation purposes. The values as pointed out previously were taken directly from the computer. In trying to estimate the degree of error in

the activity coefficient values, it is found that the error is composed of the error in the measured electromotive force and the error in E^o values due to the extrapolation. Because the $E_{obs} + \frac{2RT}{F} \ln m$ values are smoothed values, there should be and is a consistent increase in the activity coefficient values with decreasing concentration in a given system at a given temperature. On the other hand, the variation of the activity coefficient with temperature is somewhat irregular. In the 17.81 and 67.03 percent monoglyme mixtures, there is a decrease in the activity coefficients with increasing temperature. In the other systems, there is no general trend. An examination of the aqueous system in Table X ($x = 0$) and Tables A-1 through A-4 in the Appendix which contain values of other mixed solvents, points out the following trend : The activity coefficient in all cases decreases with increasing temperature. Presumably the same trend should take place in monoglyme-water systems also. Harned and coworkers (12-25) studied the cells at 5^o intervals and over a wide range of temperatures. They then smoothed the electromotive force values by plotting E_{obs} values versus the temperature. Such a smoothing of E_{obs} values would bring any divergent values into line. Since a large number of temperatures were used, the smoothed values are much better than those in this case where only four temperatures were used. Harned and Owen (3) state that an error of ±0.05 millivolts in the measured electromotive force values corresponds to an error of the order of 0.001 in the activity coefficient values. The error in $E_{obs} + \frac{2RT}{F} \ln m$ values for 8.68 and 17.81 percent monoglyme mixtures were estimated to be ±0.2mv, for 46.52 mixtures ±0.4mv,

for 67.03 percent mixtures ±1.0 millivolts and for 88.80 percent mixtures ± several millivolts. These errors transmitted to the activity coefficients results in errorsof 0.004, 0.008, 0.020 and 0.040. The values of the smoothed activity coefficients taking into account the appropriate errors are given in Table XV. It should be noted that the general trends previously mentioned all fall within the limit of experimental error in all the monoglyme-water systems. One additional observation will complete the activity coefficient discussion. A check of all mixed solvent systems shows that the mean activity coefficient of hydrochloric acid is always less than the value at the same concentration in pure water. Essentially what is being compared is the deviation from ideality, ideality being infinite dilution where it is assumed there are no ion-ion interactions. A lower dielectric constant of the solvent which corresponds to the addition of the organic solvent should result in greater deviations at the same concentration. Numerically this means that the activity coefficient is lower in the mixed solvent than in pure water. The mean activity coefficients at $0^{o}C$ in the 8.68 percent monoglyme mixtures are not given in Table XV. A re-check on the experimental data indicated that the system was not at equilibrium. The 8.68 percent system was the first one studied and the $0^{o}C$ temperature was the first temperature studied. For some reason, solutions at the lower temperature were very slow in coming to a steady state and the electromotive force values were not reproducible. However, in subsequent studies, a steady state was first attained at a higher temperature and then the

TABLE XV

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID-SMOOTHED VALUES FROM TABLE X

x = 8.68

m	15°	25°	35°
0.1	0.776	0.774	0.771
.05	.813	.812	.811
.02	.864	.864	.864
.01	.898	.898	.896
.005	.924	.924	.923
.002	.951	.950	.948
.001	.965	.964	.962

x = 17.81

m	0°	15°	25°	35°
0.1	.773	.766	.765	.761
.05	.821	.811	.805	.794
.02	.875	.865	.858	.847
.01	.906	.898	.893	.881
.005	.930	.924	.920	.913
.002	.953	.950	.947	.944
.001	.965	.963	.962	.960

TABLE XV (Cont.)

x = 46.52				
m	0°	15°	25°	35°
0.1	0.655	0.648	0.642	.640
.05	.712	.709	.706	.707
.02	.788	.787	.787	.788
.01	.839	.838	.838	.839
.005	.880	.879	.880	.879
.002	.921	.920	.920	.919
.001	.943	.942	.942	.940

x = 67.03				
m	0°	15°	25°	35°
0.1	0.46	0.44	0.43	0.42
.05	.53	.51	.50	.48
.02	.64	.63	.60	.59
.01	.72	.71	.69	.67
.005	.79	.78	.76	.74
.002	.86	.85	.83	.82
.001	.89	.89	.88	.87

TABLE XV (Cont.)

x = 88.80				
m	0^{o}	15^{o}	25^{o}	35^{o}
0.1	0.13	0.11	0.11	0.10
0.05	.16	.15	.15	.13
.02	.23	.22	.21	.19
.01	.30	.29	.29	.26
.005	.39	.39	.39	.35
.002	.52	.52	.52	.49
.001	.62	.62	.62	.59

lower temperatures. There was no trouble reproducing the measurements at $0^{o}C$ after this change was made.

Table XI in Chapter IV lists the values of the primary medium effects in the various mixed solvent systems studied. The values were calculated by means of equation (31) and are given to the correct number of significant figures. Previously the primary medium effect was given as $\ln {}^{s}_{w}\gamma_{o}$ and expressed as $\ln {}^{s}_{w}\gamma_{o\pm}$ for hydrochloric acid. The primary medium effect is simply the mean activity coefficient of hydrochloric acid at infinite dilution in the mixed solvent referred to unity at infinite dilution in pure water. The smaller values of the primary medium effects occur in systems containing the lowest percentage of monoglyme. This indicates that addition of small amounts of monoglyme does not appreciably change the behavior of the medium upon the ions at infinite dilution. However, as the percentage of monoglyme increases, the medium has a much greater effect upon ions at infinite dilution. In addition, the primary medium effect is a measure of the ease of transferring hydrogen ion and chloride ion from infinite dilution in the aqueous system to infinite dilution in the mixed solvent. The greater the percentage of monoglyme, the more work required for the transfer.

The secondary medium effects were calculated from the activity coefficients given in Table X according to equation (36). The values are given in Table XII. The values do not represent the smoothed activity coefficients as given in Table XV.

The relative partial molal heat content, $\bar{L}_{2}$, and the relative

partial molal heat capacity, $\bar{J}_2$, were calculated from equations (62) and (63) from the appropriate coefficients from Table XIII which represent equations of the form of equations (60) and (61). Only a partial list of the values are given in Table XIV. Some of the values obtained were not reasonable. There is a great deal of error involved in these values as was discussed in Chapter II. Therefore, it is not unexpected that some unreasonable results would be obtained. The values given in Table XIV,when compared with those of dioxane-water systems, show the same general trends.

SELECTED BIBLIOGRAPHY

BOOKS

1. Bates, R. G.,
Electrometric pH Determinations,
John Wiley and Sons, Inc., New York, 1954.

2. Day, M. C. and Selbin, J.,
Theoretical Inorganic Chemistry,
Reinhold Publishing Corporation, New York, 1962.

3. Harned, H. S., and Owen, B. B.,
The Physical Chemistry of Electrolytic Solutions, Third Edition,
Reinhold Publishing Corporation, New York, 1958.

4. Jordon, T. E.,
Vapor Pressure of Organic Compounds,
International Publisher, Inc.,New York, 1954.

5. Moore, W. J.,
Physical Chemistry, Second Edition,
Prentice-Hall, Inc., Engelwood Cliffs, N. J., 1962.

6. Robinson, R. A. and Stokes, R. H.,
Electrolyte Solutions,
Butterworths Scientific Publications, London, 1955.

7. Vogel, A. I.,
A Text-Book of Quantitative Inorganic Analysis; Theory and Practice,
Longmans, Green, New York and London, 1951.

SELECTED BIBLIOGRAPHY (Cont.)

PERIODICALS

8. Berns, D. S. and Fuoss, R. M., "Electrolyte-Solvent Interaction", J. Am. Chem. Soc., 82, 5585 (1960).

9. Crockford, H. D., Knight, S. B. and Staton, H. A., "Electromotive Force Studies in Dilute Solutions of Hydrochloric Acid in Aqueous Ethylene Glycol at 25°", J. Am. Chem. Soc., 72, 2164 (1950).

10. Feakins, D. and French, C. M., "E.m.f. Measurements in Acetone-Water Mixtures", J. Chem. Soc., 3168 (1956).

11. Gronwall, T. H., LaMer, V. K. and Sandved, K., "Uber den Einfluss der sogenannten höhern Glieder in der Debye-Hückelschen Theorie der Lösungen starker Electrolyte", Physik. Z., 29, 358 (1929).

12. Harned, H. S., "The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. III. Extrapolations According to the Gronwall-LaMer Extension of the Debye and Hückel Theory", J. Am. Chem. Soc., 60, 336 (1938).

13. Harned, H. S. and Allen, D. S., "Standard Potentials of Silver-Silver Chloride Cells in Some Ethanol- and Isopropyl Alcohol-Water Solutions at 25°", J. Phys. Chem., 58, 191 (1954).

14. Harned, H. S. and Calmon, C., "The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. VI. Extrapolations in 70% Dioxane Mixtures and Standard Potentials", J. Am. Chem. Soc., 60, 2130 (1938).

15. Harned, H. S. and Calmon, C., "The Properties of Electrolytes in Mixtures of Water and Organic Solvents. I. Hydrochloric Acid in Ethanol- and Isopropanol-Water Mixtures of High Dielectric Constant", J. Am. Chem. Soc., 61, 1491 (1939).

16. Harned, H. S., Calmon, C. and Donelson, J. G., "The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. VII. Properties of the 70% Dioxane Mixtures", J. Am. Chem. Soc., 60, 2133 (1938).

SELECTED BIBLIOGRAPHY (Cont.)

PERIODICALS (Cont.)

17. Harned, H. S. and Donelson, J. G.,
"The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. IV. Properties of 20% Dioxane Mixtures",
J. Am. Chem. Soc., 60, 339 (1938).

18. Harned, H. S. and Donelson, J. G.,
"The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. V. Properties of 45% Dioxane Mixtures",
J. Am. Chem. Soc., 60, 2128 (1938).

19. Harned, H. S. and Morrison, J. O.,
"The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. I. Standard Potentials",
J. Am. Chem. Soc., 58, 1908 (1936).

20. Harned, H. S., Morrison, J. O., Walker, F., Donelson, J. G. and Calman, C.,
"The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. X. General Summary and Critique",
J. Am. Chem. Soc., 61, 49 (1939).

21. Harned, H. S. and Nestler, F. H. M.,
"The Standard Potential of the Cell, $H_2|HCl(m)|AgCl\text{-}Ag$, in 50% Glycerol-Water Solutions from 0° to 90°",
J. Am. Chem. Soc., 68, 665 (1946).

22. Harned, H. S. and Thomas, H. C.,
"The Molal Electrode Potential of the Silver-Silver Chloride Electrode in Methyl Alcohol-Water Mixtures",
J. Am. Chem. Soc., 57, 1666 (1935).

23. Harned, H. S. and Thomas, H. C.,
"The Thermodynamics of Hydrochloric Acid in Methanol-Water Mixtures from Electromotive Force Measurements",
J. Am. Chem. Soc., 58, 761 (1936).

24. Harned, H. S. and Walker, F.,
"The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. IX. Properties of the 82% Dioxane Mixtures",
J. Am. Chem. Soc., 61, 48 (1939).

SELECTED BIBLIOGRAPHY (Cont.)

PERIODICALS (Cont.)

25. Harned, H. S., Walker, F. and Calmon, C., "The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. VIII. Extrapolations in 82% Dioxane Mixtures and Standard Potentials", J. Am. Chem. Soc., 61, 44 (1939).

26. Hills, G. J. and Ives, D. J. G., "The Hydrogen-Calomel Cell. Part I. The Hydrogen Electrode", J. Chem. Soc., 308 (1951).

27. Knight, S. B., Masi, J. F. and Roesel, D., "Standard Potentials of Hydrogen-Silver-Silver Chloride Cells in Ethylene Glycol Solutions at 25°", J. Am. Chem. Soc., 68, 661 (1946).

28. LaMer, V. K., Gronwall, T. H. and Greiff, L. G., "The Influence of Higher Terms of the Debye-Hückel Theory in the Case of Unsymmetric Valence Type Electrolytes", J. Phys. Chem., 35, 2245 (1931).

29. Lucasse, W. W., "The Activity Coefficients of Hydrochloric Acid in Glycerol-Water Mixtures", J. Am. Chem. Soc., 48, 626 (1926).

30. Moore, R. S. and Felsing, W. A., "The Molal Electrode Potentials of the Silver-Silver Chloride Electrode in i-Propyl Alcohol-Water Mixtures from 0 to 40°", J. Am. Chem. Soc., 69, 1076 (1947).

31. Owen, B. B., "Direct Measurement of the Primary, Secondary and Total Medium Effects of Acetic Acid", J. Am. Chem. Soc., 54, 1758 (1932).

32. Shuman, D. C. and Sen, B., "Complex Formation Thermodynamics of Some Metal (II) Phenyl-2-Pyridyl-ketoximates", Anal. chim. Acta., 33, 487 (1965).

33. Williams, J. P., Knight, S. B. and Crockford, H. D., "Electromotive Force Studies in Dilute Solutions of Hydrochloric Acid in Aqueous d-glucose Solutions", J. Am. Chem. Soc., 72, 1277 (1950).

APPENDIX

TABLE A-1

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN DIOXANE-WATER MIXTURES (3)

x = weight percent of dioxane

x = 20

m	0°	10°	25°	30°
0.1	0.736	0.729	0.720	0.716
.07	.759	.753	.740	.740
.05	.780	.774	.763	.762
.02	.835	.830	.821	.820
.01	.872	.869	.862	.861
.007	.889	.886	.880	.880
.005	.902	.900	.896	.895

x = 45

m	0°	10°	25°	30°
0.1	0.579	0.566	0.547	0.540
.07	.605	.593	.577	.570
.05	.637	.624	.607	.600
.02	.720	.707	.692	.686
.01	.776	.766	.753	.747
.005	.824	.817	.808	.803
.003	.849	.846	.842	.839

APPENDIX (Cont.)

TABLE A-1 (Cont.)

x = 70

m	0°	10°	25°	30°
0.1	0.236	0.226	0.212	0.207
.07	.259	.249	.234	.229
.05	.283	.274	.258	.253
.02	.369	.359	.342	.336
.01	.446	.436	.418	.413
.005	.530	.521	.505	.499
.003	.589	.582	.568	.563
.001	.719	.713	.700	.696

x = 82

m	5°	15°	25°	35°
.1	0.0506	0.0465	0.0429	0.0390
.07	.0563	.0521	.0484	.0441
.05	.0659	.0603	.0560	.0513
.02	.0946	.0878	.0822	.0757
.01	.1259	.1176	.1105	.1023
.005	.1674	.1561	.1479	.1380
.003	.2067	.1914	.1818	.1708
.001	.3063	.2843	.2698	.2540

TABLE A-2

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN METHANOL-WATER MIXTURES AT 0°, 25° AND 40°C (3)

N_2 = mole fraction of methanol

N_2 = 0.0588

m	0°	25°	40°
0.1	0.790	0.780	0.772
.05	.825	.819	.812
.02	.872	.866	.861
.01	.901	.897	.893
.005	.926	.922	.919
.002	.951	.948	.946
.001	.964	.962	.961

N_2 = 0.1233

m	0°	25°	40°
0.1	0.771	0.762	0.751
.05	.814	.806	.798
.02	.862	.856	.850
.01	.893	.888	.884
.005	.919	.915	.912
.002	.946	.943	.941
.001	.961	.959	.957

TABLE A-3

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES. (3)

N_2 = mole fraction of glycerol

m	N_2 = 0.01 25°	N_2 = 0.05 25°
0.1	0.798	0.775
.05	.826	.810
.02	.873	.858
.01	.902	.885
.005	.924	.898
.002	.951	----

TABLE A-4

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ETHYLENE GLYCOL-WATER MIXTURES AT 25°C. (27)

x = weight percent of ethylene glycol

m \ x	10	20	40	60
0.1	0.770	0.764	0.750	0.717
.05	.805	.799	.791	.763
.02	.851	.845	.843	.820
.01	.871	.878	.876	.858
.005	.897	.911	.908	.892
.002	----	.942	.939	.926
.001	----	.959	.957	.946

TABLE A-5

VAPOR PRESSURES OF SOLVENTS

$t^{\circ}C$	Monoglyme	Water	Acetonitrile
0	18mm	4.579mm	23mm
15	41mm	12.788mm	
25	67mm	23.756mm	
35	105mm	42.175mm	138mm

VITA

David Alfred Johnson was born March 13, 1938 at Muskegon, Michigan. He graduated from Spring Arbor, Michigan High School in June, 1956. In the Fall of 1956 he enrolled in Greenville College, Greenville, Illinois and graduated cum laude in June, 1960 with a Bachelor of Arts degree, majoring in Chemistry. In August of that year Mr. Johnson married the former Janice Derscheid of Holton, Michigan. They now have two daughters, Jacquelynn Sue and Elizabeth Ann. Mr. Johnson erolled in the Graduate School of the University of Kansas in the Fall of 1960. He returned to his alma mater in the Fall of 1962 to fill a teaching vacancy for two years. In the Summer of 1963 he was a participant in the College Teachers' Research Participation Program at Louisiana State University sponsored by the National Science Foundation. In June of 1964 he returned to Louisiana State University and is now a candidate for the Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

Candidate: David Alfred Johnson

Major Field: Chemistry

Title of Thesis: The Activity and Other Thermodynamic Properties of Hydrochloric Acid in Monoglyme - Water Mixture

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Robert V. Hansman

H B Williams

Date of Examination:

6/23/66